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(54) LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium secondary battery restraining a short circuit caused by a generation of dendrite from a negative electrode, having a high energy density, and providing an excellent charging/discharging characteristic.

SOLUTION: A lithium secondary battery has an electrolyte layer, a positive electrode, and a negative electrode made of a material containing lithium. The electrolyte layer is made of an inorganic solid electrolyte, and the positive electrode contains an organic macromolecules. The electrolyte layer preferably contains at least one type selected from a group comprising oxygen, sulfur, nitrogen, sulfide, and oxynitride. The conductivity of lithium ion of organic electrolyte of the positive electrode is preferably lower than that of the inorganic solid electrolyte of the electrolyte layer.

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CLAIMS

[Claim(s)]

[Claim 1]An electrolyte layer.

An anode.

Lithium content material.

It is the lithium secondary battery provided with the above, said electrolyte layer consists of inorganic solid electrolytes, and said anode contains an organic high polymer.

[Claim 2]The lithium secondary battery according to claim 1, wherein lithium ion conductivity at 25 ** of an electrolyte layer is more than $1 \times 10^{-5} \text{S/cm}$.

[Claim 3]The lithium secondary battery according to claim 1, wherein lithium ion conductivity at 25 ** of an electrolyte layer is more than $5 \times 10^{-4} \text{S/cm}$.

[Claim 4]The lithium secondary battery according to claim 1, wherein electrolyte layers are amorphous bodies.

[Claim 5]The lithium secondary battery according to claim 1 characterized by a thing for which an ingredient of an electrolyte layer was chosen from a group which consists of oxygen, nitrogen, a sulfide, and an oxynitride, and which contain a kind at least.

[Claim 6]A sulfide Li_2S and Li_2S , and SiS_2 . It is the compound at least with a kind chosen from a group which consists of GeS_2 and Ga_2S_3 . An oxynitride $\text{Li}_3\text{PO}_{4-X}\text{N}_{2X/3}$, $\text{Li}_4\text{SiO}_{4-X}\text{N}_{2X/3}$. The lithium secondary battery according to claim 5 characterized by at least one thing chosen from a group which consists of $\text{Li}_4\text{GeO}_{4-X}\text{N}_{2X/3}$ ($0 < X < 4$), and $\text{Li}_3\text{BO}_{3-X}\text{N}_{2X/3}$ ($0 < X < 3$).

[Claim 7]The lithium secondary battery according to claim 1, wherein an electrolyte layer contains the following ingredient.

A: more than 30 atom % -- Li ingredient B: below 65 atom % -- one or more kinds of element C:sulfur chosen from a group which consists of Lynn, silicon, boron, germanium, and gallium [Claim 8]The lithium secondary battery according to claim 7, wherein an electrolyte layer furthermore contains either [at least] oxygen or nitrogen.

[Claim 9]The lithium secondary battery according to claim 1 with which thickness of an electrolyte layer is characterized by not less than 50-nm being 50 micrometers or less.

[Claim 10]The lithium secondary battery according to claim 1, wherein an electrolyte layer comprises two-layer [of an anode side layer and a negative-electrode side layer].

[Claim 11]The lithium secondary battery according to claim 10, wherein a negative-electrode side layer is a thin film of a lithium-ion-conductivity compound containing a sulfide and an anode side layer is a thin film of a lithium-ion-conductivity compound containing an oxide.

[Claim 12]The lithium secondary battery according to claim 10 with which thickness of an electrolyte layer which consists of two-layer is characterized by thickness of an anode side layer being 0.1 micrometers or more 2 micrometers or less at not less than 2 micrometers 22 micrometers or less.

[Claim 13]The lithium secondary battery according to claim 10, wherein a negative-electrode side layer contains a lithium sulfide and a silicon sulfide and an anode side layer contains at least one side of a phosphoric acid compound and a titanate acid compound.

[Claim 14]The lithium secondary battery according to claim 10, wherein an anode side layer contains the following ingredient.

more than A:30 atom % -- Li ingredient B:Lynn C: below 50 atom % -- oxygen and nitrogen -- at least -- on the

- other hand [Claim 15]The lithium secondary battery according to claim 10, wherein thickness of an anode side layer is 50% or less more than per % of the thickness of a negative-electrode side layer.
- [Claim 16]The lithium secondary battery according to claim 10 with which thickness of an anode side layer is characterized by not less than 10-nm being 25 micrometers or less.
- [Claim 17]The lithium secondary battery according to claim 1 which furthermore carries out that ionic conductivity of this electrolyte particle is more than 10^{-3} S/cm to an anode with the feature including lithium ion conductive solid electrolyte particles.
- [Claim 18]The lithium secondary battery according to claim 1, wherein organic high polymers of an anode are disulfide system polymers of poly aniline content.
- [Claim 19]The lithium secondary battery according to claim 1, wherein an organic high polymer of an anode contains lithium salt of either LiPF_6 and LiCF_3SO_3 .
- [Claim 20]The lithium secondary battery according to claim 1, wherein an anode contains organic electrolysis liquid.
- [Claim 21]The lithium secondary battery according to claim 21 with which lithium ion conductivity of organic electrolysis liquid of an anode is characterized by being lower than lithium ion conductivity of an inorganic solid electrolyte of an electrolyte layer.
- [Claim 22]The lithium secondary battery according to claim 21 reducing ionic conductivity of organic electrolysis liquid from ionic conductivity of an inorganic solid electrolyte [near the contact portion] when organic electrolysis liquid of an anode contacts lithium content material of a negative electrode.
- [Claim 23]The lithium secondary battery according to claim 21 gasifying [near the contact portion] when an organic solvent ingredient in organic electrolysis liquid of an anode contacts lithium content material of a negative electrode.
- [Claim 24]The lithium secondary battery according to claim 21 solidifying [near the contact portion] when an organic solvent ingredient in organic electrolysis liquid of an anode contacts lithium content material of a negative electrode.
- [Claim 25]The lithium secondary battery according to claim 21 when an organic solvent ingredient in organic electrolysis liquid of an anode contacts lithium content material of a negative electrode, wherein the viscosity of organic electrolysis liquid becomes high [near the contact portion].
- [Claim 26]The lithium secondary battery according to claim 21, wherein an organic solvent ingredient in organic electrolysis liquid of an anode contains a sulfolane system compound.
- [Claim 27]The lithium secondary battery according to claim 21, wherein an organic solvent ingredient in organic electrolysis liquid of an anode contains chain carboxylate.
- [Claim 28]The lithium secondary battery according to claim 21, wherein an organic solvent ingredient in organic electrolysis liquid of an anode contains at least one kind of a compound which has a compound which has a nitrile group, and olefin binding.
- [Claim 29]The lithium secondary battery according to claim 1 with which surface roughness of a negative electrode is characterized by or more 0.01 being 5 micrometers or less with a R_{max} value.
- [Claim 30]The lithium secondary battery according to claim 1 which a metal layer which forms lithium, an alloy, or an intermetallic compound in the electrolyte layer side of a negative electrode is formed, and is characterized by this negative electrode being a multilayer or an inclination presentation.
- [Claim 31]The lithium secondary battery according to claim 1 there being no oxide layer on the surface of a negative electrode, and having a sulfide layer or a nitride layer on the surface.
- [Claim 32]The lithium secondary battery according to claim 1, wherein an electrolyte layer is directly formed in the surface of a negative electrode via an oxide layer.
- [Claim 33]The lithium secondary battery according to claim 1 having equipped each of positive and negative poles with a charge collector, and not having provided lithium content material in a negative electrode, but forming an electrolyte layer directly on a charge collector of a negative electrode.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to high capacity and a high safety lithium secondary battery. In particular, the short circuit by generating of the dendrite from a negative electrode can be controlled, and an energy density is high and it is related with the lithium secondary battery excellent in the charge-discharge cycle characteristic.

[0002]

[Description of the Prior Art]Utilization of the rechargeable lithium-ion battery which uses organic electrolysis liquid is progressing. The place by which it is characterized [the] is that unit volume or the energy output per unit weight is high as compared with other cells. In particular, utilization and development are furthered as a power supply for mobile communications, a notebook computer, and also electromobiles.

[0003]There are an organic electrolysis liquid type which impregnated the porosity polymer separator with organic electrolysis liquid, and a gel polymer type which uses the gel polymer which contained organic electrolysis liquid so much in such a lithium secondary battery.

[0004]However, an organic electrolysis liquid type and gel polymer type all are using organic electrolysis liquid so much, and have a problem resulting from the organic electrolysis liquid. That is, there is generating of withstand voltage nature, the instability to electrode material, especially the carbon usually used for a negative electrode, and gas. These organic electrolysis liquid is combustible material fundamentally, and has the danger of connecting too hastily by the temperature up and the shock by a certain cause, and exploding.

[0005]In the organic electrolysis liquid type and the gel polymer type cell, it has been a big technical technical problem to raise an energy density. It is anxious for about [300Whs/] one being a limit, and the actual condition raising one or more [400Whs/]. As the effective means, using a lithium metal for a negative electrode is examined.

[0006]However, when using lithium content material as a negative electrode, it has the influence on the electrolyte layer which the thickness of the lithium metal used for charge and discharge and the negative-electrode shape change at the time of charge and discharge give. In particular, this influence comes out by the high cycle of several 100 or more cycles. A lithium metal reacts to the moisture in the air easily, and the device for intercepting the atmosphere in stage film formation is needed.

[0007]In the lithium cell containing organic electrolysis liquid, while repeating charge and discharge, a dendrite-like lithium metal grows up to be the lithium metal surface, and this may cause an inter-electrode internal short circuit, and may cause explosion etc.

[0008]The following art is proposed as the technique of suppressing this danger.

1: Carry out the surface treatment of the lithium metal used as a negative electrode, and form a compound layer. Polymer membrane, a fluoride film, a carbonate compound film, an oxide film, etc. are mentioned to a compound layer.

[0009]2: Consider it as all the solid type batteries which do not contain the organic electrolysis liquid leading to explosion. For example, an organic high polymer, an inorganic crystal, etc. are used for an electrolyte.

[0010]

[Problem(s) to be Solved by the Invention]However, there were the following problems in each of above-mentioned art.

1-1: In the art which carries out the surface treatment of the lithium metal, what processes before constituting a cell, and the thing which makes it react to the compound in an electrolysis solution and a positive electrode

material spontaneously, and forms a compound layer when a cell is constituted are known.

[0011]1-2: In the former, it is acid treatment and plasma treatment, and the fluoride, carbonation thing, or oxide layer of lithium is formed, and it is assumed that it has the effect that they suppress growth of the dendrite of lithium at the time of charge and discharge. However, there is a problem in which generation of the hole in an interface, exfoliation of a compound layer, and growth of the intensive lithium metal to the crack and pinhole of a compound layer occur at the time of charge and discharge.

[0012]1-3: React to the lithium metal in organic electrolysis liquid about the latter, and since the substance which forms a compound layer is added, as long as the lithium metal is in contact with the electrolysis solution, form a compound layer in an interface continuously. Therefore, although a possibility that problems, such as exfoliation, will be avoided becomes high, the compound layer which is influence of the impurity component in the organic electrolysis liquid contained unescapable, and is formed in the lithium metal surface will become uneven, and the effect of suppressing growth of the dendrite of a lithium metal is thin.

[0013]2-1: Since an electrolyte is a solid, as for a total solid type, there is a problem in contact with an electrode and an electrolyte, and it cannot enlarge the current value which becomes high and can take out impedance due to the fall of this touch area, etc.

[0014]2-2: The handling of a solid electrolyte is difficult and a usage pattern has restriction. As construction material of a solid electrolyte, the oxynitride system and oxysulfide system which are a sulfide system, oxide stock, nitride systems, and such mixed stock can be considered. However, although the compound containing a sulfide has high lithium ion conductivity, it also has the fault of high hygroscopicity and hydrolysis nature simultaneously. Therefore, the handling after membrane formation of an electrolyte layer is difficult, and when finishing setting up on a cell, it poses a problem on productivity and cost that it is necessary to enclose with conveyance at an inert atmosphere and, and equipment of a glove box etc. is needed etc.

[0015]2-3: Examination of use of a lithium ion conductive solid electrolyte mainly becomes a sintered compact of bulk state, or a thing which also has the low performance of a cell and in which it is powdered, a usage pattern has a limit, and the whole ion conductivity also becomes low. On the other hand, it is difficult to control formation of a pinhole and a crack, when the electrolyte of a thin film is used. when the anode which contains organic electrolysis liquid especially is used, the electrolysis solution from an anode boils a pinhole and a crack, meets, it advances into a negative electrode surface, a dendrite grows up to be a pinhole and a crack part intensively by a reaction with a negative electrode, and the problem in which a short circuit occurs by inter-electrode arises. In addition, although a negative electrode causes a volume change in the case of charge and discharge, if current capacity per unit area is made high, resisting the stress by the distortion in that case cannot be finished, and an electrolyte layer will become is easy to be destroyed.

[0016]Therefore, the key objective of this invention controls the short circuit by generating of the dendrite from a negative electrode, and its energy density is high, and there is in providing the lithium secondary battery excellent in the charge-discharge cycle characteristic.

[0017]

[Means for Solving the Problem]An electrolyte layer constitutes this invention from an inorganic solid electrolyte, and the above-mentioned purpose is attained because an anode contains an organic high polymer. That is, growth of a dendrite on a lithium metal is prevented at the time of charge and discharge, and a reaction of organic electrolysis liquid and a negative electrode is inhibited, at the time of overcharge, a rise in heat inside a cell is suppressed and explosion can be avoided. Hereafter, each of an electrolyte layer, an anode, a negative electrode, and battery construction is explained in detail. These monograph affairs are independent, or can be combined and used.

[0018](Electrolyte layer)

It is effective in a <construction material> electrolyte layer that it is an inorganic system solid electrolyte. This is because a lithium metal and an inclination presentation volume phase are formed in an interface with a lithium metal in an inorganic solid electrolyte. That is, to having a clear interface, with an inorganic solid electrolyte, a lithium metal and an organic polymer layer formed in an interface a layer with which a lithium metal and a lithium content inorganic compound were mixed, and have prevented exfoliating with organic polymer.

[0019]As an example of an inorganic solid electrolyte, an oxynitride system and an oxysulfide system which are a sulfide system, oxide stock, nitride systems, and such mixed stock can be considered. As a sulfide here, a compound of Li_2S and Li_2S , and SiS_2 , GeS_2 , and Ga_2S_3 , etc. are mentioned. As an oxynitride, $\text{Li}_3\text{PO}_{4-X}\text{N}_{2X/3}$, and $\text{Li}_4\text{SiO}_{4-X}\text{N}_{2X/3}$, and $\text{Li}_4\text{GeO}_{4-X}\text{N}_{2X/3}$ ($0 < X < 4$), and $\text{Li}_3\text{BO}_{3-X}\text{N}_{2X/3}$ ($0 < X < 3$) is mentioned.

[0020]In the surface of a lithium metal, it becomes easy to form an inclining composition layer by containing sulfur especially. It can prevent making a crevice to an interface of a lithium metal and a solid electrolyte layer, organic electrolysis liquid's permeating in the case of a deposit and the dissolution of a lithium metal in a negative electrode at the time of charge and discharge, and a solid electrolyte layer exfoliating by this, at it.

[0021]In addition to sulfur, it also became clear by containing at least one side of oxygen and nitrogen that the effect was strengthened. Oxygen or nitrogen has high reactivity with a lithium metal, and this is for combining an inorganic solid electrolyte layer and a lithium metal more firmly. High ionic conductivity called $10^{-3} - 10^{-2} \text{S/cm}$ is realizable. This is considered to originate in polarity between elements to constitute, and an effect of distorted introduction. There are such construction material and an effect which controls especially high hygroscopicity which is a fault of an oxysulfide system.

[0022]As for lithium-elements content in these inorganic electrolyte layers, it is desirable that it is below 65 atom % above 30 atom %. By less than 30 atom %, ionic conductivity becomes low and high-resistance-izes. The adhesion of an inorganic solid electrolyte layer and a lithium metal layer falls. although the adhesion of an inorganic solid electrolyte layer and a lithium metal layer improves by presentation exceeding 65 atom % on the other hand -- an inorganic solid electrolyte layer -- polycrystal-izing -- and it porosity-izes and formation of a continuation film of a precise inorganic solid electrolyte becomes difficult. Moreover, electron conductivity is revealed, when a cell is constituted, an internal short circuit is caused, and battery capacity is reduced. Therefore, as for an electrolyte layer, it is preferred that they are amorphous bodies.

[0023]In components other than lithium of an inorganic solid electrolyte, it is preferred to contain one or more kinds of elements (these elements are hereafter called an "alloying element") chosen from a group which consists of Lynn, silicon, boron, aluminum, germanium, and gallium, and to contain sulfur. Although it is effective that they are amorphous bodies as for an inorganic solid electrolyte, the "alloying element" can constitute network structure via sulfur, and can supply a site of the size possible forming this amorphous skeleton and optimal for a lithium ion conducting. An "alloying element" can be electrified in a negative charge of the optimal intensity for catching a lithium ion which is positive charge about a sulfur atom of an end of an amorphous skeleton. That is, an end sulfur atom of this negative charge serves to help conduction of a lithium ion, without catching a lithium ion of positive charge gently moderately, and fixing firmly superfluously.

[0024]In addition to an "alloying element" and sulfur, as components other than lithium of an inorganic solid electrolyte, either [at least] oxygen or nitrogen is mentioned. Content of oxygen or nitrogen enables it to demonstrate still higher lithium ion conductivity. An effect which extends a crevice between amorphous skeletons formed is brought about, and this is presumed because hindrance which a lithium ion moves is reduced, when an oxygen atom or a nitrogen atom contains.

[0025]In addition, an inorganic solid electrolyte has improvement in the adhesion of an inorganic solid electrolyte layer and a lithium metal as an effect of containing an "alloying element." It has the performance which raises compatibility with a lithium metal further because an inorganic solid electrolyte contains an "alloying element." As already indicated, content of lithium, sulfur, oxygen, and nitrogen improves the adhesion of a lithium metal and an inorganic solid electrolyte layer, but when other elements other than an "alloying element" are contained, conversely, the compatibility of an inorganic solid electrolyte layer and a lithium metal is checked, and a tendency to become easy to exfoliate is shown.

[0026]The ionic conductivity is important for a component of a <ionic conductivity> electrolyte layer. Namely, in a Prior art, ionic conductivity of a compound layer formed by each on the surface of a lithium metal was very as low as below 10^{-7}S/cm in a room temperature. Therefore, via a pinhole and a crack which exist unescapable, even if this compound layer is a thin film which is several nanometer (nano meter) grade, Organic electrolysis liquid which has the ionic conductivity of a 10^{-3}S/cm stand infiltrates into an interface of a lithium metal and a compound layer, and a flow of a lithium ion inclines to a direction of organic electrolysis liquid of high ion conductivity. Therefore, when an interface of a lithium metal and a compound layer received erosion, exfoliation of a compound layer breaks out easily and it became clear that covering effect was thin.

[0027]On the other hand, in this invention, by forming an electrolyte layer of high ion conductivity, we decided that a flow of a lithium ion mainly passes along an electrolyte layer, and the above-mentioned problem is solved.

In 25 **, more than 10^{-5}S/cm of lithium ion conductivity of such an electrolyte layer is preferred. Carbonic acid gas ion, oxygen gas, a water molecule, or a fluorine ion contained as an impurity unescapable in an electrolysis solution even if a pinhole and a crack exist all over an electrolyte layer (thin film), A lithium metal in a pinhole or a crack reacts and layers of low ion conductivity, such as lithium carbonate, lithium oxide, and lithium fluoride, are

formed in the lithium metal surface. Therefore, a pinhole and a crack will be protected by a low ionic conduction layer, and growth of a dendrite will be controlled, and a lithium ion will mainly pass along an electrolyte layer. Ionic conductivity of a solid electrolyte layer is made still more preferably more than $5 \times 10^{-4} \text{ S/cm}$ (25 **) equivalent to not less than 10% of ionic conductivity of organic electrolysis liquid. Much more desirable lithium ion conductivity (25 **) is more than $1 \times 10^{-3} \text{ S/cm}$.

[0028] In order to form a lithium metal and a low ion-conductive compound effectively, it is also preferred to combine following at least one condition.

[0029] ** Make an organic molecule which forms carbon dioxide, a halogenide, an anionic polymerization nature organic monomer or lithium, and a compound contain positively in organic electrolysis liquid beforehand.

[0030] ** Use imide system organicity lithium etc. which are easily eluted in a fluorine compound for an electrolysis salt (solute) of organic electrolysis liquid.

[0031] ** Use disulfide system organic materials etc. which are eluted in organic electrolysis liquid in sulfur compounds for a positive electrode material.

[0032] <Two-layer structure> The above-mentioned inorganic solid electrolyte layer is considering it as two-layer structure, and the handling becomes easy further. Although a lithium-ion-conductivity compound containing a sulfide has high lithium ion conductivity as construction material of an electrolyte layer, it also has a fault of high hygroscopicity and hydrolysis nature simultaneously. On the other hand, although a lithium-ion-conductivity compound containing an oxide has the chemical stability over the atmosphere, it is an unstable compound chemically to a compound with low ion conductivity, and a lithium metal of a negative electrode. Then, make an electrolyte layer a negative-electrode side layer and two-layer [of an anode side layer], and a negative-electrode side layer considers it as a thin film of a lithium-ion-conductivity compound containing a sulfide (a lithium sulfide and a silicon sulfide), and. It becomes possible [an anode side layer is stable to the atmosphere, if it is considered as a thin film of a lithium-ion-conductivity compound containing an oxide, and] to form an electrolyte layer of high ion conductivity.

[0033] In the atmosphere, an anode side layer works as a protective film which prevents a reaction with moisture, and when constituted on a cell, it dissolves into organic electrolysis liquid. A dissolved composing element of an anode side layer reacts to a lithium metal in a pinhole and a crack in an electrolyte, forms a low ionic conduction layer, and controls intensive growth of a dendrite.

[0034] As for an anode side layer used as a protective film, it is effective that it is a lithium ion conductor which contains Lynn and contains at least one side of oxygen and nitrogen further. That is, a phosphoric acid compound or phosphoric acid nitriding **** serves as a suitable material.

[0035] As for Li ingredient of this anode side layer, it is effective that more than 30 atom % is a rate below 50 atom %. A possibility of melting at the time of the dissolution and remaining becomes high by less than 30 atom %. Hygroscopicity appears and it stops playing a role of a protective film in a presentation exceeding 50 atom %.

[0036] The thinner one of thickness of an anode side layer is preferred. However, since an effect which intercepts a negative-electrode side layer containing a sulfide from the atmosphere will decrease if too thin, not less than 10 nm or 1% or more of thickness of a negative-electrode side layer is preferred. Conversely, if an anode side layer is too thick, it will become difficult to maintain high ion conductivity, or the dissolution will become difficult.

Therefore, 25 micrometers or less or 50% or less of thickness of a negative-electrode side layer is preferred. When especially a negative-electrode side layer considers it as a thin film of a lithium-ion-conductivity compound containing a sulfide and an anode side layer considers it as a thin film of a lithium-ion-conductivity compound containing an oxide, 0.1 micrometers or more 2 micrometers or less are preferred for thickness of an anode side layer in respect of a battery characteristic.

[0037] As for thickness of the whole <thickness> electrolyte layer, it is preferred to be referred to as 50 micrometers or less at not less than 50 nm. When thickness exceeds 50 micrometers, covering effect becomes still higher, but ion conductivity worsens and reduces battery capacity. In addition, time and energy which are required for forming a film become large too much, and are not practical. In particular, resistance of ion conduction of an electrolyte layer becomes high, and a problem which cannot take large output current arises. When thickness is less than 50 nm, an ingredient of electron conductivity becomes large and a problem which becomes easy to carry out self-discharge arises. In addition, it becomes difficult to control formation of a pinhole to an electrolyte of a thin film, when an anode containing organic electrolysis liquid is used, an electrolysis solution from an anode advances into a negative electrode surface through a pinhole, and a problem which makes formation of a dendrite cause by a reaction with a negative electrode arises.

[0038] Especially thickness of the desirable whole electrolyte layer at the time of considering it as said two-layer structure is not less than 2 micrometers 22 micrometers or less. When thickness is less than 2 micrometers, it becomes difficult to control formation of a pinhole and a crack to an electrolyte of a thin film. That is, when the anode containing organic electrolysis liquid is used, an electrolysis solution from the anode infiltrates into a negative electrode surface through a pinhole and a crack, a dendrite is formed through a pinhole and a crack by a reaction with a negative electrode, and a short circuit occurs by inter-electrode. In addition, although a negative electrode causes a volume change in the case of charge and discharge, if current capacity per unit area is made high, resisting stress by distortion in that case cannot be finished, and an electrolyte layer will become is easy to be destroyed. On the other hand, when thickness exceeds 22 micrometers, a problem which cannot take large current density per unit area but to which resistance of ion conduction of an electrolyte layer becomes high, and efficiency worsens arises.

[0039] (Anode)

<Construction material> [0040] What contained an active material in a binder of an organic high polymer is suitable for construction material of an anode. Polyacrylonitrile system polymers which contain organic solvents, such as ethylene carbonate, propylene carbonate, or dimethyl carbonate, as a binder, it was chosen from a group which consists of polyethylene oxide system polymers and polyvinylidene fluoride system polymers -- a kind is preferred at least. moreover -- an active material -- Li_xCoO_2 and $\text{Li}_x\text{Mn}_2\text{O}_4$ and Li_xNiO_2 ($0 < x < 1$) -- a kind is preferred at least. In order to give electron conductivity, it is desirable to mix the end of carbon powder.

[0041] In addition, an organic high polymer in quality of a positive electrode material may be disulfide system polymers or polypyrrole system polymers of poly aniline content which has both ion conductivity and electron conductivity.

[0042] Also when above any are used for an organic high polymer, it is important to make which lithium salt of LiPF_6 and the LiCF_3SO_3 contain. Thereby, good contact with an electrolyte layer and an anode is acquired, and since resistance of an interface with an anode used as a problem in a solid electrolyte can be reduced substantially, it becomes possible to take large output current. A battery capacity fall by generating of gas which had furthermore become a problem conventionally, and neglect by overvoltage application and a charging state in the case of charge decreases greatly.

[0043] By adding lithium ion conductivity solid electrolyte powder in an anode, the amount of organic electrolysis liquid components can be reduced further, and it becomes possible to lessen a problem resulting from organic electrolysis liquid. Although it is preferred that it is the high-ion-conductivity material shown above as this solid electrolyte, what is necessary is just the material which has the ionic conductivity more than 10^{-3}S/cm .

[0044] It is difficult to remove organic electrolysis liquid from a practical standpoint on performance of a <organic electrolysis liquid in anode> cell thoroughly. However, it is possible to mainly limit to the surroundings of an active material in an anode, to make organic electrolysis liquid contain, to form an inorganic system lithium-ion-conductivity thin film on a negative electrode by using a lithium metal as a negative electrode, to double these, and to consider it as a highly efficient cell. As an advantage of this type of lithium secondary battery, there are reduction of organic electrolysis volume, control of dendritic growth of metal lithium to a negative electrode, control of contact with an anode by covering effect of a negative electrode surface, and reaction control with an electrolysis solution.

[0045] Although a still obscure point also has organic electrolysis liquid about a mechanism which gas used as a cause generates, when it contains organic electrolysis liquid, it is using battery construction of this invention, and content of organic electrolysis liquid can be substantially reduced with conventional 10% or less. Even if it neglected it by a charging state, an electrolysis solution carried out decomposition degradation like before, and it also became clear a phenomenon in which a battery characteristic falls greatly, and that it was stopped as much as possible.

[0046] When a pinhole and a crack generate to a solid electrolyte thin film, along the part, at the time of charge, a lithium metal grows intensively and tends to cause an internal short circuit. Then, even if these pinholes and a crack exist by preparing organic electrolysis liquid contained in an anode, the technique of the ability to attain a stable charging and discharging characteristic and safety is explained below.

[0047] In the first place, ionic conductivity of organic electrolysis liquid is stopped at less than it of a solid electrolyte thin film. Since Li ion is transmitted mainly through a solid electrolyte thin film layer with high ionic conductivity even if a pinhole and a crack exist, organic electrolysis liquid permeates those insides and this forms an ion conduction course, Supply of a pinhole and Li ion of KURAKUHE is suppressed and growth of metal

lithium is controlled. As well as lithium ion conductivity using organic electrolysis liquid lower than that of an inorganic solid electrolyte from the beginning, when organic electrolysis liquid of an anode contacts lithium content material of a negative electrode, [near the contact portion], ionic conductivity of organic electrolysis liquid may be reduced from ionic conductivity of an inorganic solid electrolyte.

[0048]Many things are considered by method of reducing ionic conductivity of organic electrolysis liquid. For example, a solvent whose viscosity is high like decreasing quantity of a solute of an electrolyte component or a sulfolane (Sulfolane;Tetrahydrothiophene1 and 1-dioxide) system solvent and which cannot make ion conductivity high may be used.

[0049]Organic electrolysis liquid containing an organic solvent which it is returned to the second and disassembled into it when organic electrolysis liquid contacts a lithium metal is used. It is decomposed by reduction, and this is gasificated in part, and is based on a pinhole, an effect which intercepts a Li-ion conducting route within a crack, and an effect of reducing ionic conductivity. If carboxylate is used as an organic solvent, this effect will be high and, specifically, formic acid methyl etc. will be applied.

[0050]When organic electrolysis liquid contacts the third with a lithium metal, an organic solvent in organic electrolysis liquid polymerizes by catalysis of a lithium metal, or polymerization start operation, Suppressing growth of a lithium metal is mentioned by a mechanical work of solidification or a polymer which high-viscosity-ized, reduced Li-ion conductivity and generated it, and a high viscosity object. Here, since organic electrolysis liquid will exude, it will go and these polymers and a high viscosity object will cover a pinhole and a crack part for the lithium metal surface continuously even if exfoliation of a metaphor solid electrolyte thin film breaks out, it becomes possible to constitute a very safe cell.

[0051]A thing made to contain using an anionic polymerization monomer which has olefin bindings, such as styrene, acrylonitrile, methyl acrylate, butadiene, and isoprene, is used as an organic solvent which is solidified by contact with a lithium metal and is high-viscosity-ized. It is also possible to use similarly polymerizing and solidifying and a solvent formed into a ** tone for all in part by operation of a lithium metal like acetonitrile which has a nitrile group.

[0052](Negative electrode)

Of course, as for a lithium alloy, lithium content material used for a <construction material> negative electrode is included for the lithium metal itself. As an example of a lithium alloy, an alloy with In, Ti, Zn, Bi, Sn, etc. is mentioned.

[0053]Metal thin films, such as metal which forms lithium, an alloy, or an intermetallic compound in the surface of this lithium content material, for example, aluminum, In, Bi, Zn, and Pb, may be formed. By using a negative electrode which consists of this metal thin film and lithium content material, movement of a lithium metal at the time of charge and discharge becomes smooth, and use thickness of a lithium metal increases. Modification of a negative electrode at the time of charge and discharge becomes uniform, and distortion to an electrolyte layer can be reduced. This is considered because stabilization of an interface which touches an electrolyte layer is made. An effect of smooth movement of a lithium metal or distorted reduction to an electrolyte layer will be revealed if a negative electrode has a multilayer or tilted structure. aluminum, In, Bi, Zn, Pb, etc. are comparatively stable to the atmosphere, and since this has covered a negative electrode used as a substrate at the time of electrolyte layer membrane formation, simplification of a stabilization process of production of them is attained.

[0054]The above-mentioned lithium content material may be used as it is, without performing any pretreatment, when forming an electrolyte layer. However, it is more desirable to form a thin oxide layer in the surface of metal which generally contains lithium in many cases, to once remove this oxide layer and to form a nitride layer or a sulfide layer. Thereby, an electrolyte layer can be formed in the shape of a direct lithium alloy material, and impedance of lithium content metal and a solid electrolyte layer can be reduced more. There is argon plasma processing as an elimination means of an oxide layer. Although exposing the surface of lithium content material to high frequency plasma is mentioned in a nitrogen gas atmosphere or hydrogen sulfide atmosphere as the formation technique of a nitride or a sulfide, it is not limited to this. Even if it heats after membrane formation beyond melting point temperature of a lithium metal, removal of an oxide layer on the surface of a lithium metal and formation of a sulfide layer are possible.

[0055]Surface roughness (Rmax) of a <surface roughness> negative electrode also affects performance of a cell greatly. 0.01 or more micrometers [5] or less are preferred at a Rmax value. In a case where Rmax is less than 0.01 micrometer, good junction to an electrolyte layer is not acquired, but it becomes easy to exfoliate. A deposit of a smooth lithium metal and ionization may not be performed in the case of charge and discharge. It seems that

this is related to adhesion with an electrolyte. On the other hand, if R_{\max} exceeds 5 micrometers, since it will become difficult to form a precise electrolyte layer without a pinhole, it is not desirable.

[0056](Shape and structure of a cell) A cell provided with above positive and negative poles and electrolyte layers is made into a laminated structure which put an electrolyte layer between an anode and a negative electrode, and comprises storing and obturating this layered product to a cell case. If it explains to details more, a negative electrode will be first joined to a negative pole collector, a solid electrolyte thin film of an inorganic system which does not contain organic electrolysis liquid will be formed on lithium content material used as a negative electrode, and a zygote of a negative electrode and an electrolyte will be produced. A positive electrode material containing an organic high polymer is formed on a positive pole collector (for example, copper or aluminum foil), and it is considered as an anode. These zygotes and anodes are united and a lithium secondary battery is produced. Thereby, contact resistance of a negative electrode and an anode, and an electrolyte layer can be reduced, and it becomes possible to acquire a good charging and discharging characteristic. What was made cylindrical may be used by laminating and rolling a negative electrode, an electrolyte layer, and an anode besides a button type battery laminated in this way.

[0057]A separator may be formed between an anode and a solid electrolyte layer. As construction material of a separator, it has fine pores which a lithium ion can move, and what was insoluble and was stabilized in organic electrolysis liquid is used. For example, a nonwoven fabric and a porous material which were formed from polypropylene, polyethylene, a fluoro-resin, polyamide resin, etc. can be used. In addition, a metallic-oxide film etc. which have fine pores may be sufficient.

[0058]It is not necessary to provide lithium content material in a negative electrode from the beginning, and even if it is the structure which formed an inorganic solid electrolyte layer directly on a charge collector of a negative electrode, performance of a lithium secondary battery is fully demonstrated. That is, lithium component sufficient in an anode is contained and it becomes possible to store a lithium metal between a negative pole collector and an inorganic solid electrolyte layer at the time of charge.

[0059]

[Embodiment of the Invention]Hereafter, an embodiment of the invention is described.

(Example 1-1) Thickness pasted the lithium metal foil of the same size together to 100 micrometers in thickness and copper foil (100 mm x 50 mm) used as a charge collector at 50 micrometers. As a technique to paste together, it may roll with a congruence roll. In this case, the surface accuracy of a roll needs to be smooth to the grade which can attain the surface roughness of the lithium made into the purpose. Junction also with good also carrying out temperature up to near the melting point of a lithium metal is acquired. The surface accuracy of this lithium metal was measured by STM (scanning tunneling microscope), and was $R_{\max}=0.1$ micrometer.

[0060]On this lithium metal, by the RF magnetron sputtering method, the mixture of $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_4\text{SiO}_4$ was targeted and the solid electrolyte thin film was formed in a nitrogen gas atmosphere. Thickness is 10 micrometers, the presentation of a thin film is the mole fraction as a result of EPMA (Electron Probe Micro Analyzer) analysis, and it turned out that they are Li (0.42), Si (0.13), N (0.01), O (0.01), and S (0.43). In the X diffraction, it was an amorphous state only by the halo pattern.

[0061]What heated the mixed liquor of ethylene carbonate (EC) and propylene carbonate (PC), and dissolved polyacrylonitrile (PAN) in high concentration is cooled, and EC which LiPF_6 is dissolving, and PAN which contains PC mixed liquor so much are produced. The carbon particle which gives the LiCoO_2 particles and electron conductivity used as an active material into this PAN is mixed, it applies to 300 micrometers in thickness on the aluminum foil of 100-micrometer thickness, and an anode is produced.

[0062]The lithium metal in which the solid-electrolyte membrane was formed, and the above-mentioned anode were joined, the cell was produced, the lead was taken out, and it enclosed in the aluminum lamination.

[0063]And with a current value of 100 mA conditions estimated the charging and discharging characteristic. As a result, the capacity of charge voltages in 4.2V and the discharge voltage 3.0V was 0.5Ah (amp-hr). Energy densities were 490Wh(watt-hour) /l (liter).

[0064]When 1000 cycle charges and discharges were performed on the same conditions, the fall of these characteristics was suppressed to 2%, and the trace of dendrite-like growth [lithium metal / of a negative electrode] was not seen at all. There is no generating of gas etc. and very good stability was shown.

[0065]As an active material in an anode, even if it used $\text{Li}_x\text{Mn}_2\text{O}_4$ and Li_xNiO_2 , the result was obtained almost similarly. As construction material in an anode, even if it used polyethylene oxide system polymers or

polyvinylidene fluoride system polymers, the good result was obtained similarly. The result also with same propylene carbonate or dimethyl carbonate that contains LiBF₄, LiClO₄, or LiCF₃SO₃ also as an electrolyte was obtained.

[0066](Example 1-2) In the battery construction shown in Example 1-1, as quality of a positive electrode material, it replaced with PAN system material and the disulfide system polymers of poly aniline content were used. 10 volume % mixing of the particles of the Li (0.42), Si (0.13), and O(0.01) -S (0.44) presentation whose particle diameter is 0.1 micrometer - 0.5 micrometer was done at this polymer material. Under the dry nitrogen gas atmosphere, the spraying rapid solidification of the mixed melting object of Li₂S-SiS₂-Li₄SiO₄ was carried out with the atomizing method, and this particle manufactured it. The thickness of the anode was 350 micrometers.

[0067]The charging and discharging characteristic of this cell made as an experiment was evaluated. As a result, charge voltages were set to 4.2V and capacity [in / by 50 mA discharge / the discharge voltage of 3.0V] was 0.49Ah (amp-hr). Energy densities were 400Wh(watt-hour) /l (liter). When 1000 cycle charges and discharges were performed on the same conditions, the fall of these characteristics was suppressed to 2%, and the trace of dendrite-like growth [lithium metal / of a negative electrode] was not seen at all. There is no generating of gas etc. and very good stability was shown.

[0068](Example 1-3) In the battery construction shown in Example 1-1, the thickness of an anode, an electrolyte, and a negative electrode is changed respectively, and the result of having evaluated the charging and discharging characteristic is shown in Table 1. Although it becomes possible to take the large output per unit area by thickening an electrode layer, the part and the time which charge takes become large, and they are spent on practicality. As for the thickness of not less than 2-micrometer 1000 micrometers or less and a negative electrode, 1 micrometers or more 50 micrometers or less are [the thickness of an anode] suitable for especially the thickness of 1-micrometer or more 200 micrometers or less and an electrolyte layer.

[0069]
[Table 1]

負極の 厚み (μm)	電解質 の厚み (μm)	正極の 厚み (μm)	電流容量 密度 Ah/cm ²	充電に要 する時間 (h)	充放電サイ クル劣化 (1000回)
0.1	10	0.2	0.02	0.004	
1	10	2	0.2	0.04	
10	10	20	2	0.4	
100	10	400	20	4	
500	10	1500	100	20	
50	0.04	300	10		300回で 短絡
50	1	300	10		安定
50	10	300	10		安定
50	50	300	10		安定
50	100	300	6		安定

[0070](Example 1-4) In the battery construction shown in Example 1-1, the surface roughness of a negative electrode is changed and the result of having evaluated the charging and discharging characteristic is shown in Table 2. It turns out that the membraneous quality of the electrolyte layer formed in the upper part is affected by surface roughness. That is, if the surface roughness of a negative electrode exceeds 5 micrometers, the pinhole would produce in the electrolyte layer and the charging and discharging cycle will also be short-circuited by 300 times.

[0071]
[Table 2]

負極の面粗さ (Rmax/ μ m)	電解質の 厚み (μ m)	電解質のピン ホールの有無	充放電サイク ル劣化 (1000回)
0.001	10	無し	安定
0.005	10	無し	安定
0.01	10	無し	安定
0.1	10	無し	安定
1	10	無し	安定
3	10	無し	安定
5	10	無し	安定
7	60	有り	300回で短絡

[0072](Example 1-5) In the battery construction shown in Example 1-2, after making nitriding beforehand the surface of the lithium indium alloy of a negative electrode and making a nitride layer generate, the solid-electrolyte membrane was formed similarly and the cell was produced. A presentation is Li_3N and the observation and analysis by TEM (Transmission Electron Microscope) of this nitride layer, etc. showed that that thickness was about 100 Å. This nitride layer was obtained by exposing the surface by RF plasma among a nitrogen atmosphere, before forming a solid electrolyte layer.

[0073]The charging and discharging characteristic of this cell made as an experiment was evaluated. As a result, charge voltages were set to 4.2V and capacity until voltage falls to 3.0V showed 0.49Ah (amp-hr) and a high value also in 200-mA discharge and a high current value. Energy densities were 400Wh(watt-hour) /l (liter). When 1000 cycle charges and discharges were performed on this same condition, the fall of these characteristics was suppressed to 3%, and the trace of dendrite-like growth [lithium metal / of a negative electrode] was not seen at all.

[0074](Example 2-1) Thickness makes with a substrate what pasted together the lithium metal foil (negative electrode) of the same size at 10 micrometers the charge collector which consists of copper foil (100 mm x 50 mm) at 20 micrometers in thickness. The thin film of the lithium-ion-conductivity compound containing a sulfide is formed, the thin film of the lithium-ion-conductivity compound which contains an oxide further is laminated to this lithium-metal-foil side, and the electrolyte layer of two-layer structure is formed in it. The electrolyte layer was formed by the inline-type RF magnetron sputtering method.

[0075]The mixture of $\text{Li}_2\text{S}-\text{SiS}_2$ was targeted in formation of the thin film of the lithium-ion-conductivity compound containing a sulfide, and the solid electrolyte thin film was formed in argon gas atmosphere. Thickness is 10 micrometers, the presentation of a thin film is the mole fraction as a result of EPMA (Electron Probe MicroAnalyzer) analysis, and it turned out that it is $\text{Li}:\text{Si}:\text{S}=0.42:0.13:0.45$. In the X diffraction, it was an amorphous state only by the halo pattern.

[0076]The thickness was 1 micrometer, although Li_3PO_4 was targeted and being further formed in a nitrogen atmosphere on the thin film of the lithium-ion-conductivity compound which contains a sulfide in formation of the lithium-ion-conductivity compound thin film containing an oxide.

[0077]Although this negative electrode and electrolyte layer were neglected in the atmosphere for 6 hours, change of the presentation of a sulfide layer was not seen but the very stable thing became clear. The good performance was shown without ion conductivity also reducing most high ion conductivity of a sulfide layer.

[0078]What heated the mixed liquor of ethylene carbonate (EC) and propylene carbonate (PC), and dissolved polyacrylonitrile (PAN) in high concentration was cooled, and EC which LiPF_6 is dissolving, and PAN which contains PC so much were produced. Into this PAN, the LiCoO_2 particles used as an active material and the carbon particle for which electron conductivity is given were mixed, and it applied by a thickness of 300 micrometers on the aluminum foil (positive pole collector) of 20-micrometer thickness, and was considered as the anode. And the zygote and the anode of said negative electrode and an electrolyte layer were joined, the cell was formed, and the performance was tested.

[0079]As a result, capacity until it sets charge voltages to 4.2V and voltage falls to 3.0V by 100-mA discharge was 0.5Ah (amp-hr). Energy densities were 490Wh(watt-hour) /1 (liter). When 1000 cycle charges and discharges were performed on this same condition, the fall of these characteristics was suppressed to 2%, and the trace of dendrite-like growth [lithium metal / of a negative electrode] was not seen at all. There is no generating of gas etc. and very good stability was shown.

[0080](Comparative example 2-1) Although the thickness of the thin film of the lithium-ion-conductivity compound containing a sulfide was 0.5 micrometer in Example 2-1 and the thickness of the thin film of the lithium-ion-conductivity compound containing an oxide was 5 micrometers, The oxide layer became thick too much as compared with the sulfide layer, ion conductivity got very bad, and the cell of expected performance was not obtained.

[0081]In the structure in Example 2-1, although it formed by a thickness of 1.8 micrometers by having used the thin film of the lithium-ion-conductivity compound containing an oxide as the lithium titanate system amorphous substance, other portions produced the cell of the same structure as Example 2-1 and the performance was tested, the good result was obtained.

[0082](Example 2-3)

[0083]In Example 2-1, by using the thin film of the lithium-ion-conductivity compound containing an oxide as a lithium phosphate system amorphous substance, various thickness of a sulfide layer and an oxide layer is changed, a cell is produced, and the result of having tested the performance is shown in Table 3. That O in the "battery characteristic" in front is stable also in 1000 or more cycles, at least 500 or more cycles' of O being stable, and x show not less than 5% of degradation in less than 500 cycles.

[0084]

[Table 3]

硫化物層の厚さ(μm)	酸化物層の厚さ(μm)	電池特性
2	0.1	◎
10	1	◎
15	1.7	◎
20	1.5	◎
10	2	◎
10	0.05	○
10	2.5	○
1	2.5	×
0.5	1	×
0.5	2.5	×

[0085](Example 2-4) It rolled with a congruence roll and the negative electrode which laminated 5-micrometer-thick indium metal foil to 50-micrometer-thick lithium metal foil was produced. Although diffusion set the interface of this two-layer metal mutually and the presentation was in inclination as a result of analysis, the surface was an indium simple substance.

[0086]The electrolyte layer was formed in Example 1 by the method of the statement by having made this into the substrate, the cell was produced, and the charge-and-discharge experiment was conducted on condition of 1mA[/cm]² (milliampere/square centimeter). The current capacity became 20 mAh/cm² (at the time of milliampere - /square centimeter), and almost all lithium metals also including the lithium ion which existed in the anode were used for charge and discharge. Although it went the cycle of charge and discharge by the same conditions up to 1000 cycles, there is no big change in the curve of charge and discharge, and it was stable. Generating of a dendrite etc. was not seen, either.

[0087](Example 3-1) Thickness pasted together the lithium metal foil (negative electrode) of the same size to ferrite series stainless steel foil (100 mm x 50 mm) (negative pole collector) at 10 micrometers by 20 micrometers in thickness. As a technique to paste together, it rolled with a roll.

[0088]On this lithium metal foil, by the laser ablation method, the mixture of Li₂S-SiS₂-Li₄SiO₄ was targeted and the solid electrolyte thin film was formed in argon gas atmosphere. Thickness is 10 micrometers, the presentation of a thin film is the mole fraction as a result of EPMA analysis, and it turned out that it is Li:Si:O:S=0.42:0.13:0.02:0.43. In the X diffraction, it was an amorphous state only by the halo pattern. The lithium ion conductivity of the solid electrolyte thin film was 1x10⁻³S/cm (room temperature: it is below the same).

[0089]Mix a vinylidene fluoride monomer, acetonitrile, LiPF₆, LiCoO₂ particles, and the carbon particle of a conductive auxiliary, and a polymerization initiator (oxygenation triisobutyl boron) is mixed, 100 micrometers in thickness are applied and polymerized on the aluminum foil (positive pole collector) of 20-micrometer thickness, and a gel anode is produced. The lithium ion conductivity in the organic electrolysis liquid in this anode was 5x10⁻²S/cm.

[0090]The lithium metal foil in which the solid-electrolyte membrane was formed, and the above-mentioned anode were joined, the cell was produced, the lead was taken out, and it enclosed in the aluminum lamination.

[0091]Evaluation of the charging and discharging characteristic and a crack examination were carried out. A crack examination bends the once produced cell, a solid electrolyte layer is made to produce a crack, and change of a charging and discharging characteristic is seen.

[0092]As a result, although the weak bulk leakage resulting from the pinhole in a solid electrolyte thin film was conventionally seen in the decline (80%) in current efficiency considered to be the cause in the charge-and-discharge curve of normal operation, it became the current efficiency of about 100% in the cell of this example. On the other hand, in a crack examination, the internal short circuit was not seen and most decline in current efficiency was not seen. Although the mixed solvent of propylene carbonate and dimethyl car PONETO was used for the organic solvent, the cell was produced similarly and the crack examination was done for comparison, there was almost no power surge at the time of charge, and it could not charge but it seemed that the internal short circuit has broken out.

[0093]As an active material in an anode, even if it used LiMn_2O_4 and LiNiO_2 , the result was obtained almost similarly. As construction material in an anode, even if it used polyethylene oxide system polymers or polyacrylonitrile system polymers, the good result was obtained similarly. The good result was obtained [in / as an electrolyte / any of LiBF_4 , LiClO_4 , and LiCF_3SO_3].

[0094](Example 3-2) In the battery construction shown in Example 3-1, it changed into acetonitrile and the N.N-dimethylformamide solvent (DMF) containing acrylonitrile was used. The lithium ion conductivity of the organic electrolysis liquid which uses this solvent was $2 \times 10^{-2} \text{S/cm}$.

[0095]As for the result, the same good characteristic as Example 3-1 was obtained. This result was the same even if it used styrene, acrylic ester, a methacrylonitrile, methacrylic acid ester, the butadiene derivative, and the isoprene derivative.

[0096](Example 3-3) In the battery construction shown in Example 3-1, the organic electrolysis liquid which reduced the amount of solutes of organic electrolysis liquid to usual 25% was produced, and the lithium cell was produced like Example 3-1. By reduction of the above-mentioned amount of solutes, lithium ion conductivity fell even in $5 \times 10^{-4} \text{S/cm}$.

[0097]Although the charging and discharging characteristic of this cell and the crack examination were carried out, as for current density, not less than 95% was obtained in the charge-and-discharge curve. Although the fall of some of current density was seen also by the crack examination, the characteristic was maintained mostly. Although even 500 times of cycle characteristics are the reasons for seeming the crack of the solid electrolyte thin film layer by charge and discharge conventionally and the fall of current density, etc. were seen, by the cell of the composition of this example, the fall of performance was hardly seen but the good cycle characteristic was shown.

[0098](Example 3-4) In the battery construction shown in Example 3-1, the separator was formed between the negative electrode and the anode, it changed into acetonitrile, methyl sulfolane was used, and the lithium cell was produced similarly. The lithium ion conductivity in the separator of the organic electrolysis liquid which uses this solvent was $7 \times 10^{-4} \text{S/cm}$. The same good characteristic as Example 1 was obtained, and the result showed the result also with a good cycle characteristic.

[0099](Example 3-5) In the battery construction shown in Example 3-1, it changed into acetonitrile, formic acid methyl was used, and the lithium cell was produced similarly. The lithium ion conductivity of the organic electrolysis liquid which uses this solvent was $1 \times 10^{-3} \text{S/cm}$. The same good characteristic as Example 3-1 was obtained, and the result showed the result also with a good cycle characteristic.

[0100](Example 4-1) On the charge collector which consists of a nickel metal of 1 inch diameter, the 200 micrometers (micron meter)-thick lithium metal was pasted together, and it was considered as the negative electrode. By the RF magnetron sputtering method, the mixture of Li_2S , P_2S_5 , and Li_3PO_4 was targeted and the solid electrolyte thin film was formed on this negative electrode. As for the solid-electrolyte membrane, the amorphous thing which a presentation consists of lithium 34atom%, Lynn 14atom%, sulfur 51atom%, and oxygen 1atom% became clear as a result of analysis. The thickness of this thin film was 800 nm (nano meter).

[0101]The lithium ion conductivity of this amorphous thin film was $7 \times 10^{-4} \text{S/cm}$. Ionic conductivity formed the comb type gold electrode on the glass substrate which does not contain alkaline ion, formed the thin film on it, and measured it by the complex impedance method.

[0102]The LiCoO₂ particles used as an active material, the carbon particle which gives electron conductivity, and polyvinylidene fluoride were mixed with the organic solvent, and it applied on aluminium foil, and was considered as the anode. The thickness of the active material layer was 80 micrometers, it was the capacity density of 3.5mAh (at the time of milliampere -) / cm² (square centimeter), and the total capacity was 17.2mAh.

[0103]The negative electrode which formed the solid electrolyte thin film under the argon gas atmosphere not more than dew point-60 **, A separator (porosity polymer film) and an anode are installed in piles into the hermetic container made from stainless steel, The organic electrolysis liquid in which the mixed solution of ethylene carbonate and propylene carbonate was made to dissolve 1-mol% of LiPF₆ as an electrolysis salt furthermore was dropped, and the lithium secondary battery was produced.

[0104]It is 8.6-mA constant current conditions, and the cycle experiment of charge and discharge was conducted between the charge 4.2V and the discharge 3.0V. Although the result of the cycle life was shown in Table 4, after 500 cycles, the internal short circuit was not caused and the fall of capacity was not seen, either.

[0105]
[Table 4]
無機固体電解質組成及びイオン伝導度による電池サイクル特性

		固体電解質組成（原子%：空欄は0）										イオン伝導率 (S/cm)	サイクル特性
		Li	P	Si	B	Al	Ge	Ga	S	N	O		
実施例	4-1	34	14						51		1	7×10 ⁻⁴	500 以上
	4-2	38	12						49		1	1×10 ⁻³	500 以上
	4-3	64	1						33		2	5×10 ⁻⁴	500 以上
	4-4	50	1				8		40	1		1×10 ⁻³	500 以上
	4-5	42		13					43	1	1	2×10 ⁻³	500 以上
	4-6	30			22				47		1	5×10 ⁻⁵	500 以上
	4-7	44	1				11		42	1	1	5×10 ⁻³	500 以上
	4-8	43				7		7	42		1	1×10 ⁻³	500 以上
	4-9	31	1	7			10		50		1	1×10 ⁻⁴	500 以上
	4-10	42		12					46			7×10 ⁻⁵	500 以上
比較例	4-1	-	-	-	-	-	-	-	-	-	-	-	78
	4-2	21	20						59		1	8×10 ⁻⁶	101
	4-3	66		0.3					33.7			3×10 ⁻⁶	192
	4-4	17	4					20	43		16	7×10 ⁻⁷	138
	4-5	29			29				52			4×10 ⁻⁶	251

[0106](Example 4-2 - Example 4-10) With the same composition as Example 4-1, the experiment which changed a presentation and the ion conduction characteristic of the inorganic solid electrolyte was conducted, and the cycle characteristic of this cell was investigated on the same conditions as Example 4-1. To nitrogen atom addition and content adjustment into an inorganic solid electrolyte thin film, it carried out by adjusting the nitrogen gas concentration in the introductory gas in the RF magnetron sputtering method. The result is shown in Table 4.

[0107](The comparative example 4-1 - the comparative example 4-5) The charge-and-discharge experiment was conducted with the same composition also on the case where the lithium metal which does not form the solid electrolyte layer is used as a negative electrode with the same composition as Example 4-1 as comparative experiments. The result is shown in the comparative example 4-1 of Table 4. The beginning of charge and discharge to current efficiency was as low as the level of about ninety%, and the voltage drop by which a minute internal short circuit is considered to be the cause from the time of exceeding 78 cycles came to be seen, and it fell still more nearly substantially [capacity].

[0108]In addition, the experiment with the same said of the cell by which the presentation of an inorganic solid electrolyte differs from the ion conduction characteristic was conducted, and the cycle characteristic of the cell was investigated. The result is similarly shown in Table 4. The comparative example 4-2 to 4-5 is also understood that a cycle characteristic is low.

[0109](Example 4-11 - Example 4-15) In the same composition as Example 4-1, and an inorganic solid electrolyte presentation, the experiment which changed only the thickness of the inorganic solid electrolyte thin film was conducted, and the cycle characteristic of the cell was investigated. Those results are shown in Table 5. When the thickness of the solid electrolyte layer was a range up to 50 nm - 50 micrometers, after 500 cycles, neither of

the cases caused the internal short circuit, and the fall of capacity was not seen, either.

[0110]

[Table 5]

無機固体電解質薄膜の厚みによる電池性能

		膜厚	サイクル特性
実施例	4-11	50nm	500 以上
	4-12	100nm	500 以上
	4-13	1.5 μm	500 以上
	4-14	35 μm	500 以上
	4-15	50 μm	500 以上
比較例	4-6	20nm	113
	4-7	40nm	156
	4-8	60 μm	500 以上(但し、電流効率は 95%)

[0111](The comparative example 4-6 – the comparative example 4-8) With the same composition as Example 4-1, only the thickness of Example 4-11-15 and an inorganic solid electrolyte layer was changed, the same experiment was conducted, and the cycle characteristic of the cell was investigated. The result is shown in Table 5. When the thickness of the comparative example 8 was 60 micrometers, the beginning of a charging and discharging cycle to current efficiency was as insufficient as about 95%, but change did not have 500 cycles after in the performance.

[0112](Example 4-16 – Example 4-18) The inorganic solid electrolyte layer was made into two-layer structure, the presentation of the anode side layer of the amorphous inorganic solid electrolyte layer was changed, and the stability under the atmosphere of an inorganic solid electrolyte was investigated. The battery characteristic was also investigated with the same composition as the cell explained in Example 4-1. The presentation of the inorganic solid electrolyte layer by the side of a negative electrode was considered as the same presentation as Example 4-7. Each thickness of an anode side layer and a negative-electrode side layer is 50 nm and 1 micrometer. Those results are shown in Table 6. Stability very high in any case is shown. The battery characteristic also showed expected battery capacity, the internal short circuit was not caused after 500 cycles, and the fall of capacity was not seen, either.

[0113]

[Table 6]

2層構造の無機固体電解質薄膜組成による特性変化

		正極側の層の組成(原子%)				大気中での安定性
		Li	P	O	N	
実施例	4-16	37.5	12.5	50	0	1ヶ月間変化無し
	4-17	45.5	9.8	39.4	5.3	1ヶ月間変化無し
	4-18	50	8.3	33.3	8.3	1ヶ月間変化無し
比較例	4-9	53.6	7.1	10.7	28.6	2時間後に、白濁が見られ、リチウムイオン伝導度が低下した。
	4-10	27.5	22.5	50	0	1ヶ月間変化無し ただし、充放電実験において、電流効率が低下

[0114](The comparative example 4-9 – the comparative example 4-10) The inorganic solid electrolyte layer was made into two-layer structure, the presentation of the anode side layer in an amorphous inorganic solid electrolyte layer was changed in Example 4-16-18, and the stability under the atmosphere of an inorganic solid electrolyte was investigated. The battery characteristic was also investigated with the same composition as the cell explained in Example 4-1. The presentation of the inorganic solid electrolyte by the side of a negative electrode was considered as the same presentation as Example 4-7. Those results are shown in Table 6. In those any case, it became very unstable, and the battery characteristic also fell substantially.

[0115](Example 4-19 – Example 4-20) The thickness of the anode side solid electrolyte layer in a two-layer inorganic solid electrolyte layer was changed, and the stability under the atmosphere of an inorganic solid electrolyte was investigated. The battery characteristic was investigated with the same composition as Example 4-16. The presentation of the inorganic solid electrolyte by the side of a negative electrode was considered as the same presentation as Example 4-7. The result is shown in Table 7. Stability very high in those any case was

shown. The battery characteristic also showed expected battery capacity, the internal short circuit was not caused after 500 cycles, and the fall of capacity was not seen, either.

[0116]

[Table 7]

2層構造における正極側の固体電解質層の厚みによる特性変化

		正極側の固体電解質層の厚み	大気中での安定性
実施例	4-19	10nm	1ヶ月間変化無し
	4-20	25μm	1ヶ月間変化無し
比較例	4-11	5nm	1時間後に、白濁が見られ、リチウムイオン伝導度が低下した。
	4-12	30μm	1ヶ月間変化無し ただし、充放電実験において、電流効率が低下

[0117](The comparative example 4-11 – the comparative example 4-12) As a comparative example, the inorganic solid electrolyte layer was made into two-layer structure, in Example 4-19-20, the thickness by the side of the anode of an amorphous inorganic solid electrolyte layer was changed, and the stability under the atmosphere of an inorganic solid electrolyte was investigated. The battery characteristic was also investigated with the same composition as Example 4-16. The presentation of the inorganic solid electrolyte layer by the side of a negative electrode was considered as the same presentation as Example 4-7. Those results are shown in Table 7. In those any case, it became very unstable, and battery capacity also fell substantially.

[0118](Example 4-21) The pre weld slag of the lithium metal surface of a negative electrode was once carried out in argon gas atmosphere within RF magnetron sputtering equipment, and the oxide layer which is unescapable on the lithium metal surface was removed. Then, the inorganic solid electrolyte thin film was formed on the surface. Li:39.4atom%, P:0.3atom%, B:16.0atom%, S:43.3atom%, O:1.1atom%, and the thickness of the presentation of this electrolyte layer are 2.5 micrometers. The negative electrode was used, with the same composition as Example 1, the lithium secondary battery was produced and the cycle characteristic of the cell was investigated. Although the cycle test was done on 17.2-mA constant current conditions, after 500 cycles, the internal short circuit was not caused and the fall of capacity was not seen, either.

[0119](Example 4-22) While removing the oxide layer which carries out the pre weld slag of the lithium metal surface of a negative electrode, and once exists it unescapable on the surface within RF magnetron sputtering equipment in the atmosphere containing H₂S, the lithium sulfide layer was formed. Then, the inorganic solid electrolyte thin film was formed on the surface. Li:38.2atom%, P:12.2atom%, S:48.6atom%, O:1.0atom%, and the thickness of the presentation of this electrolyte layer are 10 micrometers. The negative electrode was used, with the same composition as Example 4-1, the lithium secondary battery was produced and the cycle characteristic of the cell was investigated. Although the cycle test was done on 17.2-mA constant current conditions, after 500 cycles, the internal short circuit was not caused and the fall of capacity was not seen, either.

[0120](Example 4-23) The pre weld slag of the lithium metal surface of a negative electrode was once carried out in N₂ atmosphere within RF magnetron sputtering equipment, and while removing the oxide layer which exists unescapable on the surface, the lithium nitride layer was formed. Then, the inorganic solid electrolyte thin film was formed on the surface. Li:42.3atom%, P:0.3atom%, Si:11.8atom%, S:44.3atom%, O:1.3atom%, and the thickness of the presentation of this electrolyte layer are 1 micrometer. The negative electrode was used, with the same composition as Example 4-1, the lithium secondary battery was produced and the cycle characteristic of the cell was investigated. Although the cycle test was done on 17.2-mA constant current conditions, after 500 cycles, the internal short circuit was not caused and the fall of capacity was not seen, either.

[0121]

[Effect of the Invention]As explained above, according to this invention, the short circuit by generating of the dendrite from a lithium metal negative electrode can be controlled, and a lithium secondary battery with a high energy density, and high stability and safety excellent in the charge-discharge cycle characteristic is obtained.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention]This invention relates to high capacity and a high safety lithium secondary battery. In particular, the short circuit by generating of the dendrite from a negative electrode can be controlled, and an energy density is high and it is related with the lithium secondary battery excellent in the charge-discharge cycle characteristic.

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PRIOR ART

[Description of the Prior Art]Utilization of the rechargeable lithium-ion battery which uses organic electrolysis liquid is progressing. The place by which it is characterized [the] is that unit volume or the energy output per unit weight is high as compared with other cells. In particular, utilization and development are furthered as a power supply for mobile communications, a notebook computer, and also electromobiles.

[0003]There are an organic electrolysis liquid type which impregnated the porosity polymer separator with organic electrolysis liquid, and a gel polymer type which uses the gel polymer which contained organic electrolysis liquid so much in such a lithium secondary battery.

[0004]However, an organic electrolysis liquid type and gel polymer type all are using organic electrolysis liquid so much, and have a problem resulting from the organic electrolysis liquid. That is, there is generating of withstand voltage nature, the instability to electrode material, especially the carbon usually used for a negative electrode, and gas. These organic electrolysis liquid is combustible material fundamentally, and has the danger of connecting too hastily by the temperature up and the shock by a certain cause, and exploding.

[0005]In the organic electrolysis liquid type and the gel polymer type cell, it has been a big technical technical problem to raise an energy density. It is anxious for about [300Whs/] one being a limit, and the actual condition raising one or more [400Whs/]. As the effective means, using a lithium metal for a negative electrode is examined.

[0006]However, when using lithium content material as a negative electrode, it has the influence on the electrolyte layer which the thickness of the lithium metal used for charge and discharge and the negative-electrode shape change at the time of charge and discharge give. In particular, this influence comes out by the high cycle of several 100 or more cycles. A lithium metal reacts to the moisture in the air easily, and the device for intercepting the atmosphere in stage film formation is needed.

[0007]In the lithium cell containing organic electrolysis liquid, while repeating charge and discharge, a dendrite-like lithium metal grows up to be the lithium metal surface, and this may cause an inter-electrode internal short circuit, and may cause explosion etc.

[0008]The following art is proposed as the technique of suppressing this danger.

1: Carry out the surface treatment of the lithium metal used as a negative electrode, and form a compound layer. Polymer membrane, a fluoride film, a carbonate compound film, an oxide film, etc. are mentioned to a compound layer.

[0009]2: Consider it as all the solid type batteries which do not contain the organic electrolysis liquid leading to explosion. For example, an organic high polymer, an inorganic crystal, etc. are used for an electrolyte.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention]As explained above, according to this invention, the short circuit by generating of the dendrite from a lithium metal negative electrode can be controlled, and a lithium secondary battery with a high energy density, and high stability and safety excellent in the charge-discharge cycle characteristic is obtained.

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]However, there were the following problems in each of above-mentioned art.

1-1: In the art which carries out the surface treatment of the lithium metal, what processes before constituting a cell, and the thing which makes it react to the compound in an electrolysis solution and a positive electrode material spontaneously, and forms a compound layer when a cell is constituted are known.

[0011]1-2: In the former, it is acid treatment and plasma treatment, and the fluoride, carbonation thing, or oxide layer of lithium is formed, and it is assumed that it has the effect that they suppress growth of the dendrite of lithium at the time of charge and discharge. However, there is a problem in which generation of the hole in an interface, exfoliation of a compound layer, and growth of the intensive lithium metal to the crack and pinhole of a compound layer occur at the time of charge and discharge.

[0012]1-3: React to the lithium metal in organic electrolysis liquid about the latter, and since the substance which forms a compound layer is added, as long as the lithium metal is in contact with the electrolysis solution, form a compound layer in an interface continuously. Therefore, although a possibility that problems, such as exfoliation, will be avoided becomes high, the compound layer which is influence of the impurity component in the organic electrolysis liquid contained unescapable, and is formed in the lithium metal surface will become uneven, and the effect of suppressing growth of the dendrite of a lithium metal is thin.

[0013]2-1: Since an electrolyte is a solid, as for a total solid type, there is a problem in contact with an electrode and an electrolyte, and it cannot enlarge the current value which becomes high and can take out impedance due to the fall of this touch area, etc.

[0014]2-2: The handling of a solid electrolyte is difficult and a usage pattern has restriction. As construction material of a solid electrolyte, the oxynitride system and oxysulfide system which are a sulfide system, oxide stock, nitride systems, and such mixed stock can be considered. However, although the compound containing a sulfide has high lithium ion conductivity, it also has the fault of high hygroscopicity and hydrolysis nature simultaneously. Therefore, the handling after membrane formation of an electrolyte layer is difficult, and when finishing setting up on a cell, it poses a problem on productivity and cost that it is necessary to enclose with conveyance at an inert atmosphere and, and equipment of a glove box etc. is needed etc.

[0015]2-3: Examination of use of a lithium ion conductive solid electrolyte mainly becomes a sintered compact of bulk state, or a thing which also has the low performance of a cell and in which it is powdered, a usage pattern has a limit, and the whole ion conductivity also becomes low. On the other hand, it is difficult to control formation of a pinhole and a crack, when the electrolyte of a thin film is used. when the anode which contains organic electrolysis liquid especially is used, the electrolysis solution from an anode boils a pinhole and a crack, meets, it advances into a negative electrode surface, a dendrite grows up to be a pinhole and a crack part intensively by a reaction with a negative electrode, and the problem in which a short circuit occurs by inter-electrode arises. In addition, although a negative electrode causes a volume change in the case of charge and discharge, if current capacity per unit area is made high, resisting the stress by the distortion in that case cannot be finished, and an electrolyte layer will become is easy to be destroyed.

[0016]Therefore, the key objective of this invention controls the short circuit by generating of the dendrite from a negative electrode, and its energy density is high, and there is in providing the lithium secondary battery excellent in the charge-discharge cycle characteristic.

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MEANS

[Means for Solving the Problem]An electrolyte layer constitutes this invention from an inorganic solid electrolyte, and the above-mentioned purpose is attained because an anode contains an organic high polymer. That is, growth of a dendrite on a lithium metal is prevented at the time of charge and discharge, and a reaction of organic electrolysis liquid and a negative electrode is inhibited, at the time of overcharge, a rise in heat inside a cell is suppressed and explosion can be avoided. Hereafter, each of an electrolyte layer, an anode, a negative electrode, and battery construction is explained in detail. These monograph affairs are independent, or can be combined and used.

[0018](Electrolyte layer)

It is effective in a <construction material> electrolyte layer that it is an inorganic system solid electrolyte. This is because a lithium metal and an inclination presentation volume phase are formed in an interface with a lithium metal in an inorganic solid electrolyte. That is, to having a clear interface, with an inorganic solid electrolyte, a lithium metal and an organic polymer layer formed in an interface a layer with which a lithium metal and a lithium content inorganic compound were mixed, and have prevented exfoliating with organic polymer.

[0019]As an example of an inorganic solid electrolyte, an oxynitride system and an oxysulfide system which are a sulfide system, oxide stock, nitride systems, and such mixed stock can be considered. As a sulfide here, a compound of Li_2S and Li_2S , and SiS_2 , GeS_2 , and Ga_2S_3 , etc. are mentioned. As an oxynitride, $\text{Li}_3\text{PO}_{4-X}\text{N}_{2X/3}$, and $\text{Li}_4\text{SiO}_{4-X}\text{N}_{2X/3}$, and $\text{Li}_4\text{GeO}_{4-X}\text{N}_{2X/3}$ ($0 < X < 4$), and $\text{Li}_3\text{BO}_{3-X}\text{N}_{2X/3}$ ($0 < X < 3$) is mentioned.

[0020]In the surface of a lithium metal, it becomes easy to form an inclining composition layer by containing sulfur especially. It can prevent making a crevice to an interface of a lithium metal and a solid electrolyte layer, organic electrolysis liquid's permeating in the case of a deposit and the dissolution of a lithium metal in a negative electrode at the time of charge and discharge, and a solid electrolyte layer exfoliating by this, at it.

[0021]In addition to sulfur, it also became clear by containing at least one side of oxygen and nitrogen that the effect was strengthened. Oxygen or nitrogen has high reactivity with a lithium metal, and this is for combining an inorganic solid electrolyte layer and a lithium metal more firmly. High ionic conductivity called $10^{-3} - 10^{-2}\text{S/cm}$ is realizable. This is considered to originate in polarity between elements to constitute, and an effect of distorted introduction. There are such construction material and an effect which controls especially high hygroscopicity which is a fault of an oxysulfide system.

[0022]As for lithium-elements content in these inorganic electrolyte layers, it is desirable that it is below 65 atom % above 30 atom %. By less than 30 atom %, ionic conductivity becomes low and high-resistance-izes. The adhesion of an inorganic solid electrolyte layer and a lithium metal layer falls. although the adhesion of an inorganic solid electrolyte layer and a lithium metal layer improves by presentation exceeding 65 atom % on the other hand -- an inorganic solid electrolyte layer -- polycrystal-izing -- and it porosity-izes and formation of a continuation film of a precise inorganic solid electrolyte becomes difficult. Moreover, electron conductivity is revealed, when a cell is constituted, an internal short circuit is caused, and battery capacity is reduced. Therefore, as for an electrolyte layer, it is preferred that they are amorphous bodies.

[0023]In components other than lithium of an inorganic solid electrolyte, it is preferred to contain one or more kinds of elements (these elements are hereafter called an "alloying element") chosen from a group which consists of Lynn, silicon, boron, aluminum, germanium, and gallium, and to contain sulfur. Although it is effective that they are amorphous bodies as for an inorganic solid electrolyte, the "alloying element" can constitute network structure via sulfur, and can supply a site of the size possible forming this amorphous skeleton and optimal for a lithium ion conducting. An "alloying element" can be electrified in a negative charge of the optimal intensity for

catching a lithium ion which is positive charge about a sulfur atom of an end of an amorphous skeleton. That is, an end sulfur atom of this negative charge serves to help conduction of a lithium ion, without catching a lithium ion of positive charge gently moderately, and fixing firmly superfluously.

[0024]In addition to an "alloying element" and sulfur, as components other than lithium of an inorganic solid electrolyte, either [at least] oxygen or nitrogen is mentioned. Content of oxygen or nitrogen enables it to demonstrate still higher lithium ion conductivity. An effect which extends a crevice between amorphous skeletons formed is brought about, and this is presumed because hindrance which a lithium ion moves is reduced, when an oxygen atom or a nitrogen atom contains.

[0025]In addition, an inorganic solid electrolyte has improvement in the adhesion of an inorganic solid electrolyte layer and a lithium metal as an effect of containing an "alloying element." It has the performance which raises compatibility with a lithium metal further because an inorganic solid electrolyte contains an "alloying element." As already indicated, content of lithium, sulfur, oxygen, and nitrogen improves the adhesion of a lithium metal and an inorganic solid electrolyte layer, but when other elements other than an "alloying element" are contained, conversely, the compatibility of an inorganic solid electrolyte layer and a lithium metal is checked, and a tendency to become easy to exfoliate is shown.

[0026]The ionic conductivity is important for a component of a <ionic conductivity> electrolyte layer. Namely, in a Prior art, ionic conductivity of a compound layer formed by each on the surface of a lithium metal was very as low as below 10^{-7} S/cm in a room temperature. Therefore, via a pinhole and a crack which exist unescapable, even if this compound layer is a thin film which is several nanometer (nano meter) grade, Organic electrolysis liquid which has the ionic conductivity of a 10^{-3} S/cm stand infiltrates into an interface of a lithium metal and a compound layer, and a flow of a lithium ion inclines to a direction of organic electrolysis liquid of high ion conductivity. Therefore, when an interface of a lithium metal and a compound layer received erosion, exfoliation of a compound layer breaks out easily and it became clear that covering effect was thin.

[0027]On the other hand, in this invention, by forming an electrolyte layer of high ion conductivity, we decided that a flow of a lithium ion mainly passes along an electrolyte layer, and the above-mentioned problem is solved.

In 25 **, more than 10^{-5} S/cm of lithium ion conductivity of such an electrolyte layer is preferred. Carbonic acid gas ion, oxygen gas, a water molecule, or a fluorine ion contained as an impurity unescapable in an electrolysis solution even if a pinhole and a crack exist all over an electrolyte layer (thin film), A lithium metal in a pinhole or a crack reacts and layers of low ion conductivity, such as lithium carbonate, lithium oxide, and lithium fluoride, are formed in the lithium metal surface. Therefore, a pinhole and a crack will be protected by a low ionic conduction layer, and growth of a dendrite will be controlled, and a lithium ion will mainly pass along an electrolyte layer. Ionic conductivity of a solid electrolyte layer is made still more preferably more than 5×10^{-4} S/cm (25 **) equivalent to not less than 10% of ionic conductivity of organic electrolysis liquid. Much more desirable lithium ion conductivity (25 **) is more than 1×10^{-3} S/cm.

[0028]In order to form a lithium metal and a low ion-conductive compound effectively, it is also preferred to combine following at least one condition.

[0029]** Make an organic molecule which forms carbon dioxide, a halogenide, an anionic polymerization nature organic monomer or lithium, and a compound contain positively in organic electrolysis liquid beforehand.

[0030]** Use imide system organicity lithium etc. which are easily eluted in a fluorine compound for an electrolysis salt (solute) of organic electrolysis liquid.

[0031]** Use disulfide system organic materials etc. which are eluted in organic electrolysis liquid in sulfur compounds for a positive electrode material.

[0032]<Two-layer structure> The above-mentioned inorganic solid electrolyte layer is considering it as two-layer structure, and the handling becomes easy further. Although a lithium-ion-conductivity compound containing a sulfide has high lithium ion conductivity as construction material of an electrolyte layer, it also has a fault of high hygroscopicity and hydrolysis nature simultaneously. On the other hand, although a lithium-ion-conductivity compound containing an oxide has the chemical stability over the atmosphere, it is an unstable compound chemically to a compound with low ion conductivity, and a lithium metal of a negative electrode. Then, make an electrolyte layer a negative-electrode side layer and two-layer [of an anode side layer], and a negative-electrode side layer considers it as a thin film of a lithium-ion-conductivity compound containing a sulfide (a lithium sulfide and a silicon sulfide), and. It becomes possible [an anode side layer is stable to the atmosphere, if it is considered as a thin film of a lithium-ion-conductivity compound containing an oxide, and] to form an

electrolyte layer of high ion conductivity.

[0033]In the atmosphere, an anode side layer works as a protective film which prevents a reaction with moisture, and when constituted on a cell, it dissolves into organic electrolysis liquid. A dissolved composing element of an anode side layer reacts to a lithium metal in a pinhole and a crack in an electrolyte, forms a low ionic conduction layer, and controls intensive growth of a dendrite.

[0034]As for an anode side layer used as a protective film, it is effective that it is a lithium ion conductor which contains Lynn and contains at least one side of oxygen and nitrogen further. That is, a phosphoric acid compound or phosphoric acid nitriding ***** serves as a suitable material.

[0035]As for Li ingredient of this anode side layer, it is effective that more than 30 atom % is a rate below 50 atom %. A possibility of melting at the time of the dissolution and remaining becomes high by less than 30 atom %. Hygroscopicity appears and it stops playing a role of a protective film in a presentation exceeding 50 atom %.

[0036]The thinner one of thickness of an anode side layer is preferred. However, since an effect which intercepts a negative-electrode side layer containing a sulfide from the atmosphere will decrease if too thin, not less than 10 nm or 1% or more of thickness of a negative-electrode side layer is preferred. Conversely, if an anode side layer is too thick, it will become difficult to maintain high ion conductivity, or the dissolution will become difficult. Therefore, 25 micrometers or less or 50% or less of thickness of a negative-electrode side layer is preferred. When especially a negative-electrode side layer considers it as a thin film of a lithium-ion-conductivity compound containing a sulfide and an anode side layer considers it as a thin film of a lithium-ion-conductivity compound containing an oxide, 0.1 micrometers or more 2 micrometers or less are preferred for thickness of an anode side layer in respect of a battery characteristic.

[0037]As for thickness of the whole <thickness> electrolyte layer, it is preferred to be referred to as 50 micrometers or less at not less than 50 nm. When thickness exceeds 50 micrometers, covering effect becomes still higher, but ion conductivity worsens and reduces battery capacity. In addition, time and energy which are required for forming a film become large too much, and are not practical. In particular, resistance of ion conduction of an electrolyte layer becomes high, and a problem which cannot take large output current arises. When thickness is less than 50 nm, an ingredient of electron conductivity becomes large and a problem which becomes easy to carry out self-discharge arises. In addition, it becomes difficult to control formation of a pinhole to an electrolyte of a thin film, when an anode containing organic electrolysis liquid is used, an electrolysis solution from an anode advances into a negative electrode surface through a pinhole, and a problem which makes formation of a dendrite cause by a reaction with a negative electrode arises.

[0038]Especially thickness of the desirable whole electrolyte layer at the time of considering it as said two-layer structure is not less than 2 micrometers 22 micrometers or less. When thickness is less than 2 micrometers, it becomes difficult to control formation of a pinhole and a crack to an electrolyte of a thin film. That is, when the anode containing organic electrolysis liquid is used, an electrolysis solution from the anode infiltrates into a negative electrode surface through a pinhole and a crack, a dendrite is formed through a pinhole and a crack by a reaction with a negative electrode, and a short circuit occurs by inter-electrode. In addition, although a negative electrode causes a volume change in the case of charge and discharge, if current capacity per unit area is made high, resisting stress by distortion in that case cannot be finished, and an electrolyte layer will become is easy to be destroyed. On the other hand, when thickness exceeds 22 micrometers, a problem which cannot take large current density per unit area but to which resistance of ion conduction of an electrolyte layer becomes high, and efficiency worsens arises.

[0039](Anode)

<Construction material> [0040]What contained an active material in a binder of an organic high polymer is suitable for construction material of an anode. Polyacrylonitrile system polymers which contain organic solvents, such as ethylene carbonate, propylene carbonate, or dimethyl carbonate, as a binder, it was chosen from a group which consists of polyethylene oxide system polymers and polyvinylidene fluoride system polymers -- a kind is preferred at least. moreover -- an active material -- Li_xCoO_2 and $\text{Li}_x\text{Mn}_2\text{O}_4$ and Li_xNiO_2 ($0 < X < 1$) -- a kind is preferred at least. In order to give electron conductivity, it is desirable to mix the end of carbon powder.

[0041]In addition, an organic high polymer in quality of a positive electrode material may be disulfide system polymers or polypyrrole system polymers of poly aniline content which has both ion conductivity and electron conductivity.

[0042]Also when above any are used for an organic high polymer, it is important to make which lithium salt of LiPF_6 and the LiCF_3SO_3 contain. Thereby, good contact with an electrolyte layer and an anode is acquired, and

since resistance of an interface with an anode used as a problem in a solid electrolyte can be reduced substantially, it becomes possible to take large output current. A battery capacity fall by generating of gas which had furthermore become a problem conventionally, and neglect by overvoltage application and a charging state in the case of charge decreases greatly.

[0043]By adding lithium ion conductivity solid electrolyte powder in an anode, the amount of organic electrolysis liquid components can be reduced further, and it becomes possible to lessen a problem resulting from organic electrolysis liquid. Although it is preferred that it is the high-ion-conductivity material shown above as this solid electrolyte, what is necessary is just the material which has the ionic conductivity more than 10^{-3}S/cm .

[0044]It is difficult to remove organic electrolysis liquid from a practical standpoint on performance of a <organic electrolysis liquid in anode> cell thoroughly. However, it is possible to mainly limit to the surroundings of an active material in an anode, to make organic electrolysis liquid contain, to form an inorganic system lithium-ion-conductivity thin film on a negative electrode by using a lithium metal as a negative electrode, to double these, and to consider it as a highly efficient cell. As an advantage of this type of lithium secondary battery, there are reduction of organic electrolysis volume, control of dendritic growth of metal lithium to a negative electrode, control of contact with an anode by covering effect of a negative electrode surface, and reaction control with an electrolysis solution.

[0045]Although a still obscure point also has organic electrolysis liquid about a mechanism which gas used as a cause generates, when it contains organic electrolysis liquid, it is using battery construction of this invention, and content of organic electrolysis liquid can be substantially reduced with conventional 10% or less. Even if it neglected it by a charging state, an electrolysis solution carried out decomposition degradation like before, and it also became clear a phenomenon in which a battery characteristic falls greatly, and that it was stopped as much as possible.

[0046]When a pinhole and a crack generate to a solid electrolyte thin film, along the part, at the time of charge, a lithium metal grows intensively and tends to cause an internal short circuit. Then, even if these pinholes and a crack exist by preparing organic electrolysis liquid contained in an anode, the technique of the ability to attain a stable charging and discharging characteristic and safety is explained below.

[0047]In the first place, ionic conductivity of organic electrolysis liquid is stopped at less than it of a solid electrolyte thin film. Since Li ion is transmitted mainly through a solid electrolyte thin film layer with high ionic conductivity even if a pinhole and a crack exist, organic electrolysis liquid permeates those insides and this forms an ion conduction course, Supply of a pinhole and Li ion of KURAKUHE is suppressed and growth of metal lithium is controlled. As well as lithium ion conductivity using organic electrolysis liquid lower than that of an inorganic solid electrolyte from the beginning, when organic electrolysis liquid of an anode contacts lithium content material of a negative electrode, [near the contact portion], ionic conductivity of organic electrolysis liquid may be reduced from ionic conductivity of an inorganic solid electrolyte.

[0048]Many things are considered by method of reducing ionic conductivity of organic electrolysis liquid. For example, a solvent whose viscosity is high like decreasing quantity of a solute of an electrolyte component or a sulfolane (Sulfolane;Tetrahydrothiophene1 and 1-dioxide) system solvent and which cannot make ion conductivity high may be used.

[0049]Organic electrolysis liquid containing an organic solvent which it is returned to the second and disassembled into it when organic electrolysis liquid contacts a lithium metal is used. It is decomposed by reduction, and this is gasificated in part, and is based on a pinhole, an effect which intercepts a Li-ion conducting route within a crack, and an effect of reducing ionic conductivity. If carboxylate is used as an organic solvent, this effect will be high and, specifically, formic acid methyl etc. will be applied.

[0050]When organic electrolysis liquid contacts the third with a lithium metal, an organic solvent in organic electrolysis liquid polymerizes by catalysis of a lithium metal, or polymerization start operation, Suppressing growth of a lithium metal is mentioned by a mechanical work of solidification or a polymer which high-viscosity-ized, reduced Li-ion conductivity and generated it, and a high viscosity object. Here, since organic electrolysis liquid will exude, it will go and these polymers and a high viscosity object will cover a pinhole and a crack part for the lithium metal surface continuously even if exfoliation of a metaphor solid electrolyte thin film breaks out, it becomes possible to constitute a very safe cell.

[0051]A thing made to contain using an anionic polymerization monomer which has olefin bindings, such as styrene, acrylonitrile, methyl acrylate, butadiene, and isoprene, is used as an organic solvent which is solidified by contact with a lithium metal and is high-viscosity-ized. It is also possible to use similarly polymerizing and

solidifying and a solvent formed into a ** tone for all in part by operation of a lithium metal like acetonitrile which has a nitrile group.

[0052](Negative electrode)

Of course, as for a lithium alloy, lithium content material used for a <construction material> negative electrode is included for the lithium metal itself. As an example of a lithium alloy, an alloy with In, Ti, Zn, Bi, Sn, etc. is mentioned.

[0053]Metal thin films, such as metal which forms lithium, an alloy, or an intermetallic compound in the surface of this lithium content material, for example, aluminum, In, Bi, Zn, and Pb, may be formed. By using a negative electrode which consists of this metal thin film and lithium content material, movement of a lithium metal at the time of charge and discharge becomes smooth, and use thickness of a lithium metal increases. Modification of a negative electrode at the time of charge and discharge becomes uniform, and distortion to an electrolyte layer can be reduced. This is considered because stabilization of an interface which touches an electrolyte layer is made. An effect of smooth movement of a lithium metal or distorted reduction to an electrolyte layer will be revealed if a negative electrode has a multilayer or tilted structure. aluminum, In, Bi, Zn, Pb, etc. are comparatively stable to the atmosphere, and since this has covered a negative electrode used as a substrate at the time of electrolyte layer membrane formation, simplification of a stabilization process of production of them is attained.

[0054]The above-mentioned lithium content material may be used as it is, without performing any pretreatment, when forming an electrolyte layer. However, it is more desirable to form a thin oxide layer in the surface of metal which generally contains lithium in many cases, to once remove this oxide layer and to form a nitride layer or a sulfide layer. Thereby, an electrolyte layer can be formed in the shape of a direct lithium alloy material, and impedance of lithium content metal and a solid electrolyte layer can be reduced more. There is argon plasma processing as an elimination means of an oxide layer. Although exposing the surface of lithium content material to high frequency plasma is mentioned in a nitrogen gas atmosphere or hydrogen sulfide atmosphere as the formation technique of a nitride or a sulfide, it is not limited to this. Even if it heats after membrane formation beyond melting point temperature of a lithium metal, removal of an oxide layer on the surface of a lithium metal and formation of a sulfide layer are possible.

[0055]Surface roughness (Rmax) of a <surface roughness> negative electrode also affects performance of a cell greatly. 0.01 or more micrometers [5] or less are preferred at a Rmax value. In a case where Rmax is less than 0.01 micrometer, good junction to an electrolyte layer is not acquired, but it becomes easy to exfoliate. A deposit of a smooth lithium metal and ionization may not be performed in the case of charge and discharge. It seems that this is related to adhesion with an electrolyte. On the other hand, if Rmax exceeds 5 micrometers, since it will become difficult to form a precise electrolyte layer without a pinhole, it is not desirable.

[0056](Shape and structure of a cell) A cell provided with above positive and negative poles and electrolyte layers is made into a laminated structure which put an electrolyte layer between an anode and a negative electrode, and comprises storing and obturating this layered product to a cell case. If it explains to details more, a negative electrode will be first joined to a negative pole collector, a solid electrolyte thin film of an inorganic system which does not contain organic electrolysis liquid will be formed on lithium content material used as a negative electrode, and a zygote of a negative electrode and an electrolyte will be produced. A positive electrode material containing an organic high polymer is formed on a positive pole collector (for example, copper or aluminum foil), and it is considered as an anode. These zygotes and anodes are united and a lithium secondary battery is produced. Thereby, contact resistance of a negative electrode and an anode, and an electrolyte layer can be reduced, and it becomes possible to acquire a good charging and discharging characteristic. What was made cylindrical may be used by laminating and rolling a negative electrode, an electrolyte layer, and an anode besides a button type battery laminated in this way.

[0057]A separator may be formed between an anode and a solid electrolyte layer. As construction material of a separator, it has fine pores which a lithium ion can move, and what was insoluble and was stabilized in organic electrolysis liquid is used. For example, a nonwoven fabric and a porous material which were formed from polypropylene, polyethylene, a fluoro-resin, polyamide resin, etc. can be used. In addition, a metallic-oxide film etc. which have fine pores may be sufficient.

[0058]It is not necessary to provide lithium content material in a negative electrode from the beginning, and even if it is the structure which formed an inorganic solid electrolyte layer directly on a charge collector of a negative electrode, performance of a lithium secondary battery is fully demonstrated. That is, lithium component sufficient in an anode is contained and it becomes possible to store a lithium metal between a negative pole collector and

an inorganic solid electrolyte layer at the time of charge.

[0059]

[Embodiment of the Invention] Hereafter, an embodiment of the invention is described.

(Example 1-1) Thickness pasted the lithium metal foil of the same size together to 100 micrometers in thickness and copper foil (100 mm x 50 mm) used as a charge collector at 50 micrometers. As a technique to paste together, it may roll with a congruence roll. In this case, the surface accuracy of a roll needs to be smooth to the grade which can attain the surface roughness of the lithium made into the purpose. Junction also with good also carrying out temperature up to near the melting point of a lithium metal is acquired. The surface accuracy of this lithium metal was measured by STM (scanning tunneling microscope), and was $R_{max}=0.1$ micrometer.

[0060] On this lithium metal, by the RF magnetron sputtering method, the mixture of $Li_2S-SiS_2-Li_4SiO_4$ was targeted and the solid electrolyte thin film was formed in a nitrogen gas atmosphere. Thickness is 10 micrometers, the presentation of a thin film is the mole fraction as a result of EPMA (Electron Probe Micro Analyzer) analysis, and it turned out that they are Li (0.42), Si (0.13), N (0.01), O (0.01), and S (0.43). In the X diffraction, it was an amorphous state only by the halo pattern.

[0061] What heated the mixed liquor of ethylene carbonate (EC) and propylene carbonate (PC), and dissolved polyacrylonitrile (PAN) in high concentration is cooled, and EC which $LiPF_6$ is dissolving, and PAN which contains PC mixed liquor so much are produced. The carbon particle which gives the $LiCoO_2$ particles and electron conductivity used as an active material into this PAN is mixed, it applies to 300 micrometers in thickness on the aluminum foil of 100-micrometer thickness, and an anode is produced.

[0062] The lithium metal in which the solid-electrolyte membrane was formed, and the above-mentioned anode were joined, the cell was produced, the lead was taken out, and it enclosed in the aluminum lamination.

[0063] And with a current value of 100 mA conditions estimated the charging and discharging characteristic. As a result, the capacity of charge voltages in 4.2V and the discharge voltage 3.0V was 0.5Ah (amp-hr). Energy densities were 490Wh(watt-hour) /l (liter).

[0064] When 1000 cycle charges and discharges were performed on the same conditions, the fall of these characteristics was suppressed to 2%, and the trace of dendrite-like growth [lithium metal / of a negative electrode] was not seen at all. There is no generating of gas etc. and very good stability was shown.

[0065] As an active material in an anode, even if it used $LixMn_2O_4$ and $LixNiO_2$, the result was obtained almost similarly. As construction material in an anode, even if it used polyethylene oxide system polymers or polyvinylidene fluoride system polymers, the good result was obtained similarly. The result also with same propylene carbonate or dimethyl carbonate that contains $LiBF_4$, $LiClO_4$, or $LiCF_3SO_3$ also as an electrolyte was obtained.

[0066] (Example 1-2) In the battery construction shown in Example 1-1, as quality of a positive electrode material, it replaced with PAN system material and the disulfide system polymers of poly aniline content were used. 10 volume % mixing of the particles of the Li (0.42), Si (0.13), and O(0.01) -S (0.44) presentation whose particle diameter is 0.1 micrometer - 0.5 micrometer was done at this polymer material. Under the dry nitrogen gas atmosphere, the spraying rapid solidification of the mixed melting object of $Li_2S-SiS_2-Li_4SiO_4$ was carried out with the atomizing method, and this particle manufactured it. The thickness of the anode was 350 micrometers.

[0067] The charging and discharging characteristic of this cell made as an experiment was evaluated. As a result, charge voltages were set to 4.2V and capacity [in / by 50 mA discharge / the discharge voltage of 3.0V] was 0.49Ah (amp-hr). Energy densities were 400Wh(watt-hour) /l (liter). When 1000 cycle charges and discharges were performed on the same conditions, the fall of these characteristics was suppressed to 2%, and the trace of dendrite-like growth [lithium metal / of a negative electrode] was not seen at all. There is no generating of gas etc. and very good stability was shown.

[0068] (Example 1-3) In the battery construction shown in Example 1-1, the thickness of an anode, an electrolyte, and a negative electrode is changed respectively, and the result of having evaluated the charging and discharging characteristic is shown in Table 1. Although it becomes possible to take the large output per unit area by thickening an electrode layer, the part and the time which charge takes become large, and they are spent on practicality. As for the thickness of not less than 2-micrometer 1000 micrometers or less and a negative electrode, 1 micrometers or more 50 micrometers or less are [the thickness of an anode] suitable for especially the thickness of 1-micrometer or more 200 micrometers or less and an electrolyte layer.

[0069]

[Table 1]

負極の厚み (μm)	電解質の厚み (μm)	正極の厚み (μm)	電流容量密度 Ah/cm ²	充電に要する時間 (h)	充放電サイクル劣化 (1000回)
0.1	10	0.2	0.02	0.004	
1	10	2	0.2	0.04	
10	10	20	2	0.4	
100	10	400	20	4	
500	10	1500	100	20	
50	0.04	300	10		300回で短絡
50	1	300	10		安定
50	10	300	10		安定
50	50	300	10		安定
50	100	300	6		安定

[0070](Example 1-4) In the battery construction shown in Example 1-1, the surface roughness of a negative electrode is changed and the result of having evaluated the charging and discharging characteristic is shown in Table 2. It turns out that the membraneous quality of the electrolyte layer formed in the upper part is affected by surface roughness. That is, if the surface roughness of a negative electrode exceeds 5 micrometers, the pinhole would produce in the electrolyte layer and the charging and discharging cycle will also be short-circuited by 300 times.

[0071]

[Table 2]

負極の面粗さ (Rmax/μm)	電解質の厚み (μm)	電解質のピンホールの有無	充放電サイクル劣化 (1000回)
0.001	10	無し	安定
0.005	10	無し	安定
0.01	10	無し	安定
0.1	10	無し	安定
1	10	無し	安定
3	10	無し	安定
5	10	無し	安定
7	60	有り	300回で短絡

[0072](Example 1-5) In the battery construction shown in Example 1-2, after making nitriding beforehand the surface of the lithium indium alloy of a negative electrode and making a nitride layer generate, the solid-electrolyte membrane was formed similarly and the cell was produced. A presentation is Li₃N and the observation and analysis by TEM (Transmission Electron Microscope) of this nitride layer, etc. showed that that thickness was about 100 Å. This nitride layer was obtained by exposing the surface by RF plasma among a nitrogen atmosphere, before forming a solid electrolyte layer.

[0073]The charging and discharging characteristic of this cell made as an experiment was evaluated. As a result, charge voltages were set to 4.2V and capacity until voltage falls to 3.0V showed 0.49Ah (amp-hr) and a high value also in 200-mA discharge and a high current value. Energy densities were 400Wh(watt-hour) /l (liter). When 1000 cycle charges and discharges were performed on this same condition, the fall of these characteristics was suppressed to 3%, and the trace of dendrite-like growth [lithium metal / of a negative electrode] was not seen at all.

[0074](Example 2-1) Thickness makes with a substrate what pasted together the lithium metal foil (negative electrode) of the same size at 10 micrometers the charge collector which consists of copper foil (100 mm x 50 mm) at 20 micrometers in thickness. The thin film of the lithium-ion-conductivity compound containing a sulfide is formed, the thin film of the lithium-ion-conductivity compound which contains an oxide further is laminated to this lithium-metal-foil side, and the electrolyte layer of two-layer structure is formed in it. The electrolyte layer was formed by the inline-type RF magnetron sputtering method.

[0075]The mixture of Li₂S-SiS₂ was targeted in formation of the thin film of the lithium-ion-conductivity

compound containing a sulfide, and the solid electrolyte thin film was formed in argon gas atmosphere. Thickness is 10 micrometers, the presentation of a thin film is the mole fraction as a result of EPMA (Electron Probe MicroAnalyzer) analysis, and it turned out that it is Li:Si:S=0.42:0.13:0.45. In the X diffraction, it was an amorphous state only by the halo pattern.

[0076]The thickness was 1 micrometer, although Li_3PO_4 was targeted and being further formed in a nitrogen atmosphere on the thin film of the lithium-ion-conductivity compound which contains a sulfide in formation of the lithium-ion-conductivity compound thin film containing an oxide.

[0077]Although this negative electrode and electrolyte layer were neglected in the atmosphere for 6 hours, change of the presentation of a sulfide layer was not seen but the very stable thing became clear. The good performance was shown without ion conductivity also reducing most high ion conductivity of a sulfide layer.

[0078]What heated the mixed liquor of ethylene carbonate (EC) and propylene carbonate (PC), and dissolved polyacrylonitrile (PAN) in high concentration was cooled, and EC which LiPF_6 is dissolving, and PAN which

contains PC so much were produced. Into this PAN, the LiCoO_2 particles used as an active material and the carbon particle for which electron conductivity is given were mixed, and it applied by a thickness of 300 micrometers on the aluminum foil (positive pole collector) of 20-micrometer thickness, and was considered as the anode. And the zygote and the anode of said negative electrode and an electrolyte layer were joined, the cell was formed, and the performance was tested.

[0079]As a result, capacity until it sets charge voltages to 4.2V and voltage falls to 3.0V by 100-mA discharge was 0.5Ah (amp-hr). Energy densities were 490Wh(watt-hour) /1 (liter). When 1000 cycle charges and discharges were performed on this same condition, the fall of these characteristics was suppressed to 2%, and the trace of dendrite-like growth [lithium metal / of a negative electrode] was not seen at all. There is no generating of gas etc. and very good stability was shown.

[0080](Comparative example 2-1) Although the thickness of the thin film of the lithium-ion-conductivity compound containing a sulfide was 0.5 micrometer in Example 2-1 and the thickness of the thin film of the lithium-ion-conductivity compound containing an oxide was 5 micrometers, The oxide layer became thick too much as compared with the sulfide layer, ion conductivity got very bad, and the cell of expected performance was not obtained.

[0081]In the structure in Example 2-1, although it formed by a thickness of 1.8 micrometers by having used the thin film of the lithium-ion-conductivity compound containing an oxide as the lithium titanate system amorphous substance, other portions produced the cell of the same structure as Example 2-1 and the performance was tested, the good result was obtained.

[0082](Example 2-3)

[0083]In Example 2-1, by using the thin film of the lithium-ion-conductivity compound containing an oxide as a lithium phosphate system amorphous substance, various thickness of a sulfide layer and an oxide layer is changed, a cell is produced, and the result of having tested the performance is shown in Table 3. That O in the "battery characteristic" in front is stable also in 1000 or more cycles, at least 500 or more cycles' of O being stable, and x show not less than 5% of degradation in less than 500 cycles.

[0084]

[Table 3]

硫化物層の厚さ(μm)	酸化物層の厚さ(μm)	電池特性
2	0.1	◎
10	1	◎
15	1.7	◎
20	1.5	◎
10	2	◎
10	0.05	○
10	2.5	○
1	2.5	×
0.5	1	×
0.5	2.5	×

[0085](Example 2-4) It rolled with a congruence roll and the negative electrode which laminated 5-micrometer-thick indium metal foil to 50-micrometer-thick lithium metal foil was produced. Although diffusion set the

interface of this two-layer metal mutually and the presentation was in inclination as a result of analysis, the surface was an indium simple substance.

[0086]The electrolyte layer was formed in Example 1 by the method of the statement by having made this into the substrate, the cell was produced, and the charge-and-discharge experiment was conducted on condition of $1\text{mA}/\text{cm}^2$ (milliampere/square centimeter). The current capacity became $20\text{mAh}/\text{cm}^2$ (at the time of milliampere - /square centimeter), and almost all lithium metals also including the lithium ion which existed in the anode were used for charge and discharge. Although it went the cycle of charge and discharge by the same conditions up to 1000 cycles, there is no big change in the curve of charge and discharge, and it was stable. Generating of a dendrite etc. was not seen, either.

[0087](Example 3-1) Thickness pasted together the lithium metal foil (negative electrode) of the same size to ferrite series stainless steel foil (100 mm x 50 mm) (negative pole collector) at 10 micrometers by 20 micrometers in thickness. As a technique to paste together, it rolled with a roll.

[0088]On this lithium metal foil, by the laser ablation method, the mixture of $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_4\text{SiO}_4$ was targeted and the solid electrolyte thin film was formed in argon gas atmosphere. Thickness is 10 micrometers, the presentation of a thin film is the mole fraction as a result of EPMA analysis, and it turned out that it is $\text{Li}:\text{Si}:\text{O}:\text{S}=0.42:0.13:0.02:0.43$. In the X diffraction, it was an amorphous state only by the halo pattern. The lithium ion conductivity of the solid electrolyte thin film was $1\times 10^{-3}\text{S}/\text{cm}$ (room temperature: it is below the same).

[0089]Mix a vinylidene fluoride monomer, acetonitrile, LiPF_6 , LiCoO_2 particles, and the carbon particle of a conductive auxiliary, and a polymerization initiator (oxygenation triisobutyl boron) is mixed, 100 micrometers in thickness are applied and polymerized on the aluminum foil (positive pole collector) of 20-micrometer thickness, and a gel anode is produced. The lithium ion conductivity in the organic electrolysis liquid in this anode was $5\times 10^{-2}\text{S}/\text{cm}$.

[0090]The lithium metal foil in which the solid-electrolyte membrane was formed, and the above-mentioned anode were joined, the cell was produced, the lead was taken out, and it enclosed in the aluminum lamination.

[0091]Evaluation of the charging and discharging characteristic and a crack examination were carried out. A crack examination bends the once produced cell, a solid electrolyte layer is made to produce a crack, and change of a charging and discharging characteristic is seen.

[0092]As a result, although the weak bulk leakage resulting from the pinhole in a solid electrolyte thin film was conventionally seen in the decline (80%) in current efficiency considered to be the cause in the charge-and-discharge curve of normal operation, it became the current efficiency of about 100% in the cell of this example. On the other hand, in a crack examination, the internal short circuit was not seen and most decline in current efficiency was not seen. Although the mixed solvent of propylene carbonate and dimethyl car PONETO was used for the organic solvent, the cell was produced similarly and the crack examination was done for comparison, there was almost no power surge at the time of charge, and it could not charge but it seemed that the internal short circuit has broken out.

[0093]As an active material in an anode, even if it used $\text{Li}_x\text{Mn}_2\text{O}_4$ and Li_xNiO_2 , the result was obtained almost similarly. As construction material in an anode, even if it used polyethylene oxide system polymers or polyacrylonitrile system polymers, the good result was obtained similarly. The good result was obtained [in / as an electrolyte / any of LiBF_4 , LiClO_4 , and LiCF_3SO_3].

[0094](Example 3-2) In the battery construction shown in Example 3-1, it changed into acetonitrile and the N.N-dimethylformamide solvent (DMF) containing acrylonitrile was used. The lithium ion conductivity of the organic electrolysis liquid which uses this solvent was $2\times 10^{-2}\text{S}/\text{cm}$.

[0095]As for the result, the same good characteristic as Example 3-1 was obtained. This result was the same even if it used styrene, acrylic ester, a methacrylonitrile, methacrylic acid ester, the butadiene derivative, and the isoprene derivative.

[0096](Example 3-3) In the battery construction shown in Example 3-1, the organic electrolysis liquid which reduced the amount of solutes of organic electrolysis liquid to usual 25% was produced, and the lithium cell was produced like Example 3-1. By reduction of the above-mentioned amount of solutes, lithium ion conductivity fell even in $5\times 10^{-4}\text{S}/\text{cm}$.

[0097]Although the charging and discharging characteristic of this cell and the crack examination were carried out, as for current density, not less than 95% was obtained in the charge-and-discharge curve. Although the fall

of some of current density was seen also by the crack examination, the characteristic was maintained mostly. Although even 500 times of cycle characteristics are the reasons for seeming the crack of the solid electrolyte thin film layer by charge and discharge conventionally and the fall of current density, etc. were seen, by the cell of the composition of this example, the fall of performance was hardly seen but the good cycle characteristic was shown.

[0098](Example 3-4) In the battery construction shown in Example 3-1, the separator was formed between the negative electrode and the anode, it changed into acetonitrile, methyl sulfolane was used, and the lithium cell was produced similarly. The lithium ion conductivity in the separator of the organic electrolysis liquid which uses this solvent was $7 \times 10^{-4} \text{S/cm}$. The same good characteristic as Example 1 was obtained, and the result showed the result also with a good cycle characteristic.

[0099](Example 3-5) In the battery construction shown in Example 3-1, it changed into acetonitrile, formic acid methyl was used, and the lithium cell was produced similarly. The lithium ion conductivity of the organic electrolysis liquid which uses this solvent was $1 \times 10^{-3} \text{S/cm}$. The same good characteristic as Example 3-1 was obtained, and the result showed the result also with a good cycle characteristic.

[0100](Example 4-1) On the charge collector which consists of a nickel metal of 1 inch diameter, the 200 micrometers (micron meter)-thick lithium metal was pasted together, and it was considered as the negative electrode. By the RF magnetron sputtering method, the mixture of Li_2S , P_2S_5 , and Li_3PO_4 was targeted and the solid electrolyte thin film was formed on this negative electrode. As for the solid-electrolyte membrane, the amorphous thing which a presentation consists of lithium 34atom%, Lynn 14atom%, sulfur 51atom%, and oxygen 1atom% became clear as a result of analysis. The thickness of this thin film was 800 nm (nano meter).

[0101]The lithium ion conductivity of this amorphous thin film was $7 \times 10^{-4} \text{S/cm}$. Ionic conductivity formed the comb type gold electrode on the glass substrate which does not contain alkaline ion, formed the thin film on it, and measured it by the complex impedance method.

[0102]The LiCoO_2 particles used as an active material, the carbon particle which gives electron conductivity, and polyvinylidene fluoride were mixed with the organic solvent, and it applied on aluminium foil, and was considered as the anode. The thickness of the active material layer was 80 micrometers, it was the capacity density of 3.5mAh (at the time of milliampere -) / cm^2 (square centimeter), and the total capacity was 17.2mAh.

[0103]The negative electrode which formed the solid electrolyte thin film under the argon gas atmosphere not more than dew point-60 **, A separator (porosity polymer film) and an anode are installed in piles into the hermetic container made from stainless steel, The organic electrolysis liquid in which the mixed solution of ethylene carbonate and propylene carbonate was made to dissolve 1-mol% of LiPF_6 as an electrolysis salt furthermore was dropped, and the lithium secondary battery was produced.

[0104]It is 8.6-mA constant current conditions, and the cycle experiment of charge and discharge was conducted between the charge 4.2V and the discharge 3.0V. Although the result of the cycle life was shown in Table 4, after 500 cycles, the internal short circuit was not caused and the fall of capacity was not seen, either.

[0105]

[Table 4]

無機固体電解質組成及びイオン伝導度による電池サイクル特性

		固体電解質組成（原子％：空欄は 0）										イオン伝導率 (S/cm)	サイクル特性
		Li	P	Si	B	Al	Ge	Ga	S	N	O		
実施例	4-1	34	14						51		1	7×10^{-4}	500 以上
	4-2	38	12						49		1	1×10^{-3}	500 以上
	4-3	64	1						33		2	5×10^{-4}	500 以上
	4-4	50	1				8		40	1		1×10^{-3}	500 以上
	4-5	42		13					43	1	1	2×10^{-3}	500 以上
	4-6	30			22				47		1	5×10^{-5}	500 以上
	4-7	44	1				11		42	1	1	5×10^{-3}	500 以上
	4-8	43				7		7	42		1	1×10^{-3}	500 以上
	4-9	31	1	7			10		50		1	1×10^{-4}	500 以上
	4-10	42		12					46			7×10^{-5}	500 以上
比較例	4-1	-	-	-	-	-	-	-	-	-	-	-	78
	4-2	21	20						59		1	8×10^{-6}	101
	4-3	66		0.3					33.7			3×10^{-6}	192
	4-4	17	4					20	43		16	7×10^{-7}	138
	4-5	29			29				52			4×10^{-6}	251

[0106](Example 4-2 – Example 4-10) With the same composition as Example 4-1, the experiment which changed a presentation and the ion conduction characteristic of the inorganic solid electrolyte was conducted, and the cycle characteristic of this cell was investigated on the same conditions as Example 4-1. To nitrogen atom addition and content adjustment into an inorganic solid electrolyte thin film, it carried out by adjusting the nitrogen gas concentration in the introductory gas in the RF magnetron sputtering method. The result is shown in Table 4.

[0107](The comparative example 4-1 – the comparative example 4-5) The charge-and-discharge experiment was conducted with the same composition also on the case where the lithium metal which does not form the solid electrolyte layer is used as a negative electrode with the same composition as Example 4-1 as comparative experiments. The result is shown in the comparative example 4-1 of Table 4. The beginning of charge and discharge to current efficiency was as low as the level of about ninety%, and the voltage drop by which a minute internal short circuit is considered to be the cause from the time of exceeding 78 cycles came to be seen, and it fell still more nearly substantially [capacity].

[0108]In addition, the experiment with the same said of the cell by which the presentation of an inorganic solid electrolyte differs from the ion conduction characteristic was conducted, and the cycle characteristic of the cell was investigated. The result is similarly shown in Table 4. The comparative example 4-2 to 4-5 is also understood that a cycle characteristic is low.

[0109](Example 4-11 – Example 4-15) In the same composition as Example 4-1, and an inorganic solid electrolyte presentation, the experiment which changed only the thickness of the inorganic solid electrolyte thin film was conducted, and the cycle characteristic of the cell was investigated. Those results are shown in Table 5. When the thickness of the solid electrolyte layer was a range up to 50 nm – 50 micrometers, after 500 cycles, neither of the cases caused the internal short circuit, and the fall of capacity was not seen, either.

[0110]

[Table 5]

無機固体電解質薄膜の厚みによる電池性能

		膜厚	サイクル特性
実施例	4-11	50nm	500 以上
	4-12	100nm	500 以上
	4-13	1.5 μm	500 以上
	4-14	35 μm	500 以上
	4-15	50 μm	500 以上
比較例	4-6	20nm	113
	4-7	40nm	156
	4-8	60 μm	500 以上(但し、電流効率は 95%)

[0111](The comparative example 4-6 – the comparative example 4-8) With the same composition as Example 4-1,

only the thickness of Example 4-11-15 and an inorganic solid electrolyte layer was changed, the same experiment was conducted, and the cycle characteristic of the cell was investigated. The result is shown in Table 5. When the thickness of the comparative example 8 was 60 micrometers, the beginning of a charging and discharging cycle to current efficiency was as insufficient as about 95%, but change did not have 500 cycles after in the performance. [0112](Example 4-16 - Example 4-18) The inorganic solid electrolyte layer was made into two-layer structure, the presentation of the anode side layer of the amorphous inorganic solid electrolyte layer was changed, and the stability under the atmosphere of an inorganic solid electrolyte was investigated. The battery characteristic was also investigated with the same composition as the cell explained in Example 4-1. The presentation of the inorganic solid electrolyte layer by the side of a negative electrode was considered as the same presentation as Example 4-7. Each thickness of an anode side layer and a negative-electrode side layer is 50 nm and 1 micrometer. Those results are shown in Table 6. Stability very high in any case is shown. The battery characteristic also showed expected battery capacity, the internal short circuit was not caused after 500 cycles, and the fall of capacity was not seen, either.

[0113]

[Table 6]

2層構造の無機固体電解質薄膜組成による特性変化

		正極側の層の組成(原子%)				大気中での安定性
		Li	P	O	N	
実施例	4-16	37.5	12.5	50	0	1ヶ月間変化無し
	4-17	45.5	9.8	39.4	5.3	1ヶ月間変化無し
	4-18	50	8.3	33.3	8.3	1ヶ月間変化無し
比較例	4-9	53.6	7.1	10.7	28.6	2時間後に、白濁が見られ、リチウムイオン伝導度が低下した。
	4-10	27.5	22.5	50	0	1ヶ月間変化無し ただし、充放電実験において、電流効率が低下

[0114](The comparative example 4-9 - the comparative example 4-10) The inorganic solid electrolyte layer was made into two-layer structure, the presentation of the anode side layer in an amorphous inorganic solid electrolyte layer was changed in Example 4-16-18, and the stability under the atmosphere of an inorganic solid electrolyte was investigated. The battery characteristic was also investigated with the same composition as the cell explained in Example 4-1. The presentation of the inorganic solid electrolyte by the side of a negative electrode was considered as the same presentation as Example 4-7. Those results are shown in Table 6. In those any case, it became very unstable, and the battery characteristic also fell substantially.

[0115](Example 4-19 - Example 4-20) The thickness of the anode side solid electrolyte layer in a two-layer inorganic solid electrolyte layer was changed, and the stability under the atmosphere of an inorganic solid electrolyte was investigated. The battery characteristic was investigated with the same composition as Example 4-16. The presentation of the inorganic solid electrolyte by the side of a negative electrode was considered as the same presentation as Example 4-7. The result is shown in Table 7. Stability very high in those any case was shown. The battery characteristic also showed expected battery capacity, the internal short circuit was not caused after 500 cycles, and the fall of capacity was not seen, either.

[0116]

[Table 7]

2層構造における正極側の固体電解質層の厚みによる特性変化

		正極側の固体電解質層の厚み	大気中での安定性
実施例	4-19	10nm	1ヶ月間変化無し
	4-20	25μm	1ヶ月間変化無し
比較例	4-11	5nm	1時間後に、白濁が見られ、リチウムイオン伝導度が低下した。
	4-12	30μm	1ヶ月間変化無し ただし、充放電実験において、電流効率が低下

[0117](The comparative example 4-11 - the comparative example 4-12) As a comparative example, the inorganic

solid electrolyte layer was made into two-layer structure, in Example 4-19-20, the thickness by the side of the anode of an amorphous inorganic solid electrolyte layer was changed, and the stability under the atmosphere of an inorganic solid electrolyte was investigated. The battery characteristic was also investigated with the same composition as Example 4-16. The presentation of the inorganic solid electrolyte layer by the side of a negative electrode was considered as the same presentation as Example 4-7. Those results are shown in Table 7. In those any case, it became very unstable, and battery capacity also fell substantially.

[0118](Example 4-21) The pre weld slag of the lithium metal surface of a negative electrode was once carried out in argon gas atmosphere within RF magnetron sputtering equipment, and the oxide layer which is unescapable on the lithium metal surface was removed. Then, the inorganic solid electrolyte thin film was formed on the surface. Li:39.4atom%, P:0.3atom%, B:16.0atom%, S:43.3atom%, O:1.1atom%, and the thickness of the presentation of this electrolyte layer are 2.5 micrometers. The negative electrode was used, with the same composition as Example 1, the lithium secondary battery was produced and the cycle characteristic of the cell was investigated. Although the cycle test was done on 17.2-mA constant current conditions, after 500 cycles, the internal short circuit was not caused and the fall of capacity was not seen, either.

[0119](Example 4-22) While removing the oxide layer which carries out the pre weld slag of the lithium metal surface of a negative electrode, and once exists it unescapable on the surface within RF magnetron sputtering equipment in the atmosphere containing H₂S, the lithium sulfide layer was formed. Then, the inorganic solid electrolyte thin film was formed on the surface. Li:38.2atom%, P:12.2atom%, S:48.6atom%, O:1.0atom%, and the thickness of the presentation of this electrolyte layer are 10 micrometers. The negative electrode was used, with the same composition as Example 4-1, the lithium secondary battery was produced and the cycle characteristic of the cell was investigated. Although the cycle test was done on 17.2-mA constant current conditions, after 500 cycles, the internal short circuit was not caused and the fall of capacity was not seen, either.

[0120](Example 4-23) The pre weld slag of the lithium metal surface of a negative electrode was once carried out in N₂ atmosphere within RF magnetron sputtering equipment, and while removing the oxide layer which exists unescapable on the surface, the lithium nitride layer was formed. Then, the inorganic solid electrolyte thin film was formed on the surface. Li:42.3atom%, P:0.3atom%, Si:11.8atom%, S:44.3atom%, O:1.3atom%, and the thickness of the presentation of this electrolyte layer are 1 micrometer. The negative electrode was used, with the same composition as Example 4-1, the lithium secondary battery was produced and the cycle characteristic of the cell was investigated. Although the cycle test was done on 17.2-mA constant current conditions, after 500 cycles, the internal short circuit was not caused and the fall of capacity was not seen, either.

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

WRITTEN AMENDMENT

----- [Written amendment]

[Filing date] June 28, Heisei 12 (2000.6.28)

[Amendment 1]

[Document to be Amended] Specification

[Item(s) to be Amended] Claim

[Method of Amendment] Change

[Proposed Amendment]

[Claim(s)]

[Claim 1] In a lithium secondary battery provided with an electrolyte layer, an anode, and a negative electrode that consists of lithium content material,

Said electrolyte layer consists of inorganic solid electrolytes,

A lithium secondary battery, wherein said anode contains an organic high polymer.

[Claim 2] The lithium secondary battery according to claim 1, wherein lithium ion conductivity at 25 ** of an electrolyte layer is more than $1 \times 10^{-5} \text{ S/cm}$.

[Claim 3] The lithium secondary battery according to claim 1, wherein lithium ion conductivity at 25 ** of an electrolyte layer is more than $5 \times 10^{-4} \text{ S/cm}$.

[Claim 4] The lithium secondary battery according to claim 1, wherein electrolyte layers are amorphous bodies.

[Claim 5] The lithium secondary battery according to claim 1 characterized by a thing for which an ingredient of an electrolyte layer was chosen from a group which consists of oxygen, nitrogen, a sulfide, and an oxynitride, and which contain a kind at least.

[Claim 6] A sulfide is a compound at least with a kind chosen from a group which consists of Li_2S and Li_2S , SiS_2 , GeS_2 , and Ga_2S_3 ,

An oxynitride $\text{Li}_3\text{PO}_{4-X}\text{N}_{2X/3}$, $\text{Li}_4\text{SiO}_{4-X}\text{N}_{2X/3}$, The lithium secondary battery according to claim 5 characterized by at least one thing chosen from a group which consists of $\text{Li}_4\text{GeO}_{4-X}\text{N}_{2X/3}$ ($0 < X < 4$), and $\text{Li}_3\text{BO}_{3-X}\text{N}_{2X/3}$ ($0 < X < 3$).

[Claim 7] The lithium secondary battery according to claim 1, wherein an electrolyte layer contains the following ingredient.

A: More than 30 atom % is Li ingredient below 65 atom %.

B: One or more kinds of elements chosen from a group which consists of Linn, silicon, boron, germanium, and gallium

C: Sulfur

[Claim 8] The lithium secondary battery according to claim 7, wherein an electrolyte layer furthermore contains either [at least] oxygen or nitrogen.

[Claim 9] The lithium secondary battery according to claim 1 with which thickness of an electrolyte layer is characterized by not less than 50-nm being 50 micrometers or less.

[Claim 10] The lithium secondary battery according to claim 1, wherein an electrolyte layer comprises two-layer [of an anode side layer and a negative-electrode side layer].

[Claim 11] A negative-electrode side layer is a thin film of a lithium-ion-conductivity compound containing a sulfide,

The lithium secondary battery according to claim 10, wherein an anode side layer is a thin film of a lithium-ion-conductivity compound containing an oxide.

[Claim 12] Thickness of an electrolyte layer which consists of two-layer is not less than 2 micrometers 22 micrometers or less,

The lithium secondary battery according to claim 10 with which thickness of an anode side layer is characterized by 0.1-micrometer or more being 2 micrometers or less.

[Claim 13] A negative-electrode side layer contains a lithium sulfide and a silicon sulfide,

The lithium secondary battery according to claim 10, wherein an anode side layer contains at least one side of a phosphoric acid compound and a titanate acid compound.

[Claim 14] The lithium secondary battery according to claim 10, wherein an anode side layer contains the following ingredient.

More than A:30 atom % is Li ingredient below 50 atom %.

B: Lynn

C: oxygen and nitrogen -- at least -- on the other hand

[Claim 15] The lithium secondary battery according to claim 10, wherein thickness of an anode side layer is 50% or less more than per % of the thickness of a negative-electrode side layer.

[Claim 16] The lithium secondary battery according to claim 10 with which thickness of an anode side layer is characterized by not less than 10-nm being 25 micrometers or less.

[Claim 17] Furthermore, lithium ion conductive solid electrolyte particles are included in an anode,

The lithium secondary battery according to claim 1, wherein ionic conductivity of this electrolyte particle is more than 10^{-3} S/cm.

[Claim 18] The lithium secondary battery according to claim 1, wherein organic high polymers of an anode are disulfide system polymers of poly aniline content.

[Claim 19] The lithium secondary battery according to claim 1, wherein an organic high polymer of an anode contains lithium salt of either LiPF_6 and LiCF_3SO_3 .

[Claim 20] The lithium secondary battery according to claim 1, wherein an anode contains organic electrolysis liquid.

[Claim 21] The lithium secondary battery according to claim 20 with which lithium ion conductivity of organic electrolysis liquid of an anode is characterized by being lower than lithium ion conductivity of an inorganic solid electrolyte of an electrolyte layer.

[Claim 22] The lithium secondary battery according to claim 20 reducing ionic conductivity of organic electrolysis liquid from ionic conductivity of an inorganic solid electrolyte [near the contact portion] when organic electrolysis liquid of an anode contacts lithium content material of a negative electrode.

[Claim 23] The lithium secondary battery according to claim 20 gasifying [near the contact portion] when an organic solvent ingredient in organic electrolysis liquid of an anode contacts lithium content material of a negative electrode.

[Claim 24] The lithium secondary battery according to claim 20 solidifying [near the contact portion] when an organic solvent ingredient in organic electrolysis liquid of an anode contacts lithium content material of a negative electrode.

[Claim 25] The lithium secondary battery according to claim 20 when an organic solvent ingredient in organic electrolysis liquid of an anode contacts lithium content material of a negative electrode, wherein the viscosity of organic electrolysis liquid becomes high [near the contact portion].

[Claim 26] The lithium secondary battery according to claim 20, wherein an organic solvent ingredient in organic electrolysis liquid of an anode contains a sulfolane system compound.

[Claim 27] The lithium secondary battery according to claim 20, wherein an organic solvent ingredient in organic electrolysis liquid of an anode contains chain carboxylate.

[Claim 28] The lithium secondary battery according to claim 20, wherein an organic solvent ingredient in organic electrolysis liquid of an anode contains at least one kind of a compound which has a nitrile group, and olefin binding.

[Claim 29] The lithium secondary battery according to claim 1 with which surface roughness of a negative electrode is characterized by or more 0.01 being 5 micrometers or less with a R_{max} value.

[Claim 30] A metal layer which forms lithium, an alloy, or an intermetallic compound in the electrolyte layer side of a negative electrode is formed,

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The lithium secondary battery according to claim 1, wherein this negative electrode is a multilayer or an inclination presentation.

[Claim 31]The lithium secondary battery according to claim 1 there being no oxide layer on the surface of a negative electrode, and having a sulfide layer or a nitride layer on the surface.

[Claim 32]The lithium secondary battery according to claim 1, wherein an electrolyte layer is directly formed in the surface of a negative electrode via an oxide layer.

[Claim 33]The lithium secondary battery according to claim 1 having equipped each of positive and negative poles with a charge collector, and not having provided lithium content material in a negative electrode, but forming an electrolyte layer directly on a charge collector of a negative electrode.

[Translation done.]